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VOLUME XXXVIII JANUARY 1959 No. 1

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FUEL

A QUARTERLY JOURNAL OF FUEL SCIENCE

General Editor for *Combustion and Flame* and *Fuel*
SIR ALFRED EGERTON, F.R.S.

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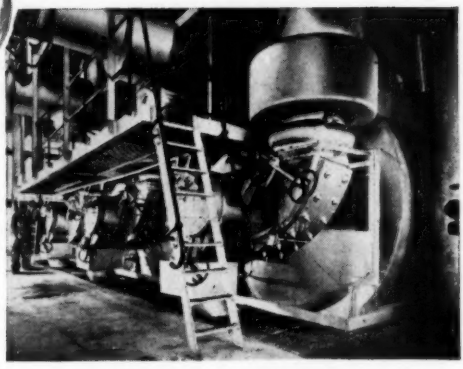

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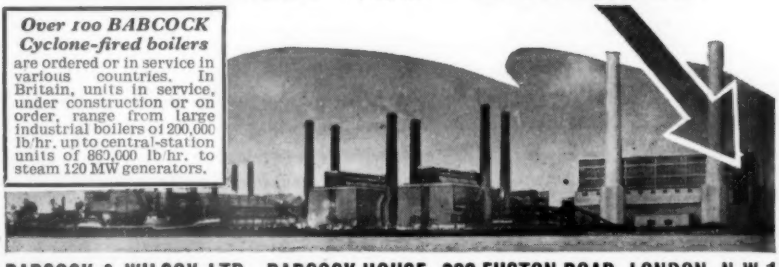

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Published quarterly. Annual subscription including postage—U.K. £5 5s. 0d.; U.S.A. $16.00. Combined subscription with COMBUSTION AND FLAME*—U.K. £8 8s. 0d.; U.S.A. $25.00. Editorial Offices, Showroom, Binding and Trade Departments*: 4–5 Bell Yard, Temple Bar, London, W.C.2. *Publishing and Advertisement Offices*: 88 Kingsway, London, W.C.2. *Telephone*: Holborn 6900. *U.S.A. Distributors: Interscience Publishers Inc., 250 Fifth Avenue, New York 1, N.Y.*

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FUEL

A Quarterly Journal of Fuel Science

Editorial At the end of the year just completed, Sir ALFRED EGERTON, under pressure from his many other duties, relinquished the Editorship of this Journal after guiding it for ten years. His unusual combination of experience in the academic and Governmental aspects of fuel policy and fuel research enabled him worthily to uphold and develop the standards set by his predecessors, from Professor WHEELER to Drs LESSING, FIELDNER and MOTT. It was at Sir ALFRED'S insistence that the format and the style were changed to accord more closely with those of journals in other fields of science. Though Sir ALFRED will continue as General Editor of *Fuel* and *Combustion and Flame*, in order to coordinate the contents of the two journals, he will no longer exercise the normal editorial powers in respect of *Fuel*, and all concerned with this Journal will wish to record at this time their appreciation of the great services he has rendered and of his wise guidance during his tenure of the Editorial chair.

Among the events of the year may be mentioned the Sheffield Conference on 'Science in the Use of Coal' convened by the Institute of Fuel in April and the meeting of the World Power Conference at Montreal in September. We much regret to record the death of Dr MARIE STOPES in October; an appreciation of her work on coal by Dr LESSING is to be found on p 104.

It is appropriate this year that the customary January Editorial should restate the policy of the Journal, and, at a time when uncertainties as to trends in the use of fuel are even greater than normal, attempt to look into its future.

Fuel is by definition a Journal of Fuel *Science* and is not intended as a medium for publishing descriptions of plant or plant results, except when the latter make a contribution to scientific understanding. The work described should possess novelty. Repetition of earlier work, even though on a different series of fuels, can in general satisfy this requirement only if it leads to new and unexpected conclusions.

Though *Fuel* is not directly concerned with industrial plant, the type of paper published is influenced by the industrial situation and corresponding research objectives, as well as by the natural advance of knowledge. Papers on entirely new subjects may be found in our future pages, emphasizing the increasingly wide range of fuels used; since this is largely a research Journal, the papers published may reflect the fuel pattern 10 to 20 years ahead of the date of publication rather than the current pattern. How can this be predicted? The answer is that it cannot; but without recapitulating the previous Editorial articles we can consider what is practically possible, or in the words of E. F. SCHUMACHER* 'make exploratory calculations'. An exploratory

*Private meeting of Royal Statistical Society, May 1958.

calculation can itself be scientific but in using the results to decide, for example, research policy, intuitive judgment must be used and the implementation of the decision represents a calculated risk.

Among the chief factors that affect the future pattern of fuel usage are the basic ones of supply and technique; in addition, political, economic and strategic factors and the incidence of novel discoveries.

Basic factors include the quantity and type of fuels to which we have ready access and the flexibility with which we can obtain and use them. The British coal industry is, at this stage of its technical development, particularly inflexible in output and this can lead to shortage, as until recently, and to sudden and unexpected surplus as with small coal. Political factors can exert a stabilizing influence. For example, the unemployment that would attend a sudden reduction in coal consumption is some insurance against any political move likely to entail this. Another political factor of great current importance is the Clean Air Act. Dominant among economic factors are the prospects of industrial expansion, stability or recession. We have seen recently how estimates of future fuel consumption made in the middle of this decade are already outdated because they were based on an assumed expansion in production of some $3\frac{1}{2}$ per cent per annum, whereas in fact there has been some recession. Other economic factors influence the relative use of solid fuel, fluid fuel or electricity; in times of prosperity price may be less important than convenience in use. Strategic factors largely determine the availability of oil (and possibly uranium), and, since they are so uncertain, must favour planning for future flexibility.

The rate of progress of the nuclear power programme is clearly determined in part by political and economic considerations and its very existence is a warning against too confident prediction: in 1939 the present situation would scarcely have been foreseen at all. Plans and recommendations relating to the use of oil have frequently been modified owing to the changing interplay of politics, economics and strategy.

Economic determinants must include not only the total price or cost relations between various fuels but also the relative capital investment required to secure unit output. It is reasonable to ask whether energy from nuclear fusion can ever be as cheap as has been predicted. Even with heavy water from the sea, the capital and running costs might place a high minimum value on the electricity produced.

Having considered the situation in principle, it is now worth while examining how far the conflicting predictions and the uncertainties of today can be reduced in practice to provide policy guidance and clear expectations.

Forecasts of the trend of energy consumption have, for the most part, been based on the assumption of a continuing increase in industrial production, commonly 3 to $3\frac{1}{2}$ per cent per annum compounded, which is often taken to imply a 2 per cent per annum increase in energy needs allowing for improved fuel efficiency. Besides considering the world as a whole, it is useful to contrast requirements for the U.S.A. and the U.K. since these countries are not far different in industrial maturity though very differently placed in

natural resources. Oil is at present the chief fuel in the United States, coal in Britain. The requirements of Britain are being met as far as possible by rapid development of nuclear energy; additional coal would be hard to come by and imported oil involves risk. In the U.S.A. industrial exploitation of nuclear energy is expected to be slow until this becomes truly competitive with coal and oil; the reserves and potential production increase of coal are so large that reliance is being placed on this fuel together with oil and natural gas for almost the whole of the expected increase in requirements. Nuclear energy in 1975 may well contribute less in absolute amount in the U.S.A. than in Great Britain and in the former will probably not affect the balance of the coal industry at all.

Forecasts are hazardous; but we can proceed on the assumption that a decrease in standard of living would be resisted politically at all costs and that the commonly assumed increase represents a maximum. The atomic energy plans for Great Britain are fairly firm and to some extent already in hand, and the increases forecast for coal production, if needed, are quite small. The chief doubt in this country therefore attaches to the demand for oil. The energy gap produced by an increase of 2 per cent per annum could not be met until after 1975 by any practicable further acceleration of the nuclear energy programme. 1975 may therefore see the use of 200 to 240 million tons of coal; some 65 million tons coal equivalent from nuclear energy allowing for the latest acceleration in the programme; and oil sufficient for transport only as a minimum, or 80 million tons coal equivalent on semi-official forecasts of total energy, or 150 million tons (i.e. 90 to 100 million tons weight of oil) according to some industrial sources including the oil companies. Recent opinion has tended towards the more conservative estimates. In the U.S.A. in 1975 consumption of coal may lie between 400 and 750 million *long** tons, that of oil and natural gas between 900 and 1 500 million long tons coal equivalent. In both countries notable increases are expected in coal for electrical power production and, especially in the U.K., for coke-making.

Further guidance may be obtained by considering the limitations of investment resources and of reserves of fossil fuel. An interesting analysis of proposed capital investment in the fuel industries for Great Britain was contributed to *The Banker* for February, 1957, by J. E. HARTSHORN. The average capital investment required to obtain an extra ton of coal a year is £12†; for crude oil £20 and for fuel oil after transport and refining £35 to £40. It is well known that conventional power stations cost about £50 per kW installed, nuclear power stations £120 together with £30 for the initial fuel charge. The total investment for electricity at point of sale, including the primary fuel investment and that for transmission equipment, is estimated by Hartshorn as £115 to £125 per kW for coal-fired stations†, £160 to £170 for oil-fired stations and £190 for nuclear power stations. Since nuclear energy costs have more margin for reduction than the others (a reduction to £100 per kW for the power station alone has been quoted) the total investment as between oil and nuclear power generation is likely to become roughly equal in the near future, but installation costs for both may be substantially greater

* 2 240 lb. † May be higher with internal transport.

than for generation from coal. Potentially, conventional power stations have a longer life than nuclear ones, but against this must be set the limited availability of extra coal and the dangers of reliance on oil. Sir CHRISTOPHER HINTON has shown [*Nature, Lond.* 18 October (1958) 1047] that electricity from nuclear power stations should cost 0·66 to 0·70*d* per unit, two thirds of this representing capital charges, compared with 0·54*d* per unit for conventional stations, about one third representing capital charges. Even if no charge were made for the nuclear fuel, the price per unit would be unlikely to fall below 0·4*d*. The nuclear energy cost moreover is based on the assumption of a high load factor, about 75 per cent, whereas on the accelerated programme nuclear power output is likely to exceed the base load by 1971–72. Capital costs will presumably have to be reduced* even below £100 per kW in stations designed to start work after that date. This is the chief 'if' in the immediate programme. At least one of the new stations (Trawsfynydd) is to be combined with a pumped storage hydroelectric plant to reduce variations in generator output. The question remains whether coal-fired stations will still be built after 1970 to handle peak load.

The total planned investment in the fuel industries for 1956–65 is discussed by Hartshorn in relation to the above specific costs. This is scarcely affected by the acceleration of the nuclear power programme, and amounts to about £4 600 million at 1955 prices—a very large call on our resources amounting in the writer's estimation to about 15 per cent of the corresponding national investment capacity. About one fifth of this total is likely to be invested in coal production, one quarter each in conventional and nuclear power stations. These totals accord fairly closely in proportion with actual and approved expenditure for 1956–58 as published in the recent White Paper on this subject (*Command 415*, April 1958).

The chief danger to be avoided is competition between oil and coal, on the basis of price and convenience alone, for the non-nuclear energy demand between, say, 1960 and 1980. If oil were to 'win' temporarily, coal production capacity that would later prove vitally necessary might be lost. It is essential that this situation be avoided. Production of oil and gas from coal is an obvious answer and one much favoured at present. The South African SASOL plant has cost about £200 per ton a year of potential oil production (compare £20 for natural oil) and the necessary investment may well prove eventually some £100 even in more recent schemes. Oil from coal is therefore far from becoming economically competitive; if the official projection of oil requirements in 1975—some 50 million tons per annum—were all made from coal the investment required on the present showing would double the already heavy fuel investment figure mentioned earlier! But cost is not all, and some such step seems essential to our welfare. A. H. A. WYNN of the N.C.B. has proposed that installation of nuclear power stations and of pressure gasifiers for making synthesis gas should proceed in step for the most effective results. Production of cheap non-toxic gas would help considerably.

The prospective oil/coal conflict brings us to the question of reserves. The last hundred years has seen a complete reversal in the relative proportions of

* 20 to 30 per cent?—See COCKCROFT, Sir JOHN, *Nature, Lond.* 182 (15 November 1958) 1334.

currently renewed and fossil fuels used with the result that exhaustion of the latter is now a limiting factor that begins to affect planning.

Oil and natural gas are the first to be affected. Only a world view of these commodities has any relevance. Oil is always near exhaustion on proved reserves, and a time must come when the rate of new discoveries ceases to keep pace with annual consumption. On post-war estimates (e.g. P.E.P. 'Report on World Population and Resources, 1955') world reserves of oil and natural gas would last until between A.D. 2000 and 2700—2000 if no nuclear contribution to world energy is taken into account and energy demand increases at 3½ per cent a year; 2700 if the present rate of use failed to increase and full advantage were taken of projected nuclear energy developments. An intermediate forecast which assumes 2 per cent per annum expansion of world energy and allows for the nuclear contribution gives oil a life until the year 2070 but ignores the industrialization of under-developed countries unless at the expense of the others. Even allowing for the recent finds in the Sahara region and the optimism of O.E.E.C. over reserves within Western Europe, we may reasonably expect an absolute crisis in oil supplies around the middle of the next century. Corresponding estimates for oil resources within the U.S.A. alone give a life of only 10 to 20 years (and Britain has virtually no oil), so that strategic supply problems are likely to become even more acute. If some oil is to be conserved for purposes other than combustion an agreed world decision should be made by 1975.

World coal is in a much stronger position and should last 1 500 years on reasonable expectations. Coal in the U.S.A. should last at least 200 to 800 years depending on whether the rapid rate of increase in consumption predicted in the Paley *Report* is maintained, say, until the year 2000, or is not realized. British coal is likely to last for hundreds of years but the rate of production may fall by about one per cent a year after 1970, leading perhaps to a serious coal shortage by the year 2050.

The position of coking coals calls for special comment. In British coke ovens the coals chiefly used are the N.C.B.'s rank coding groups 301 to 600. The blend charged to the coke oven should contain not more than about 1·5 per cent of sulphur and unfortunately, before cleaning, it is groups 400 to 600 that are liable to contain the highest percentages of this element. This seriously limits the fraction of their production that can be used to make coke—in practice not much more than half without cleaning. At present, however, only some 40 per cent of the low sulphur coals in the 301 to 500 groups are used for metallurgical coke-making together with about 25 per cent of the 600 group. There would seem to be a margin of some 11 million tons between production of the 301 and 400 groups and their present allocation to coke ovens; in the 500 and higher groups the coke oven requirements overlap with those of the gas retort so that the position is less clear. Allowing for diversion of the 301 and 400 groups from other markets, production should at least cope with demand until 1975. If all of the 301 to 500 and a quarter of the 600 group production, excepting the output with excessive sulphur and ash content, were available for coke ovens there might be at present a 20 million ton safety margin each year, though this would decrease slowly. The reserves of coking coals in Britain are adequate if properly husbanded and

put to best use; there should be no serious problem before 1975 but there may be later if coke ovens continue to be essential to iron production.

In the U.S.A. (H. E. RISSER, *The Mines Magazine*, July 1958) those seams now chiefly used for coke-making would have a lifetime of only 70 to 90 years if consumption were stabilized, 45 to 60 years allowing for 2 per cent growth in consumption each year. Supplies of these coals are likely to be seriously limited by production capacity after 1975–80 and according to Risser even doubling reserves would scarcely change this date. There is likely to be a trend towards new constituents for coking blends, e.g. the Illinois coals.

Another important question is the availability of domestic smokeless fuels in Great Britain for implementing the Clean Air Act. The tendency of the gas industry, dictated by the need to cheapen gas supplies, to use more oil or imported methane as raw material and later to gasify coal completely, means that solid smokeless fuel, already none too plentiful in the new situation*, is likely to become scarcer. Alternative solid smokeless fuels would have to be reasonably cheap; cheaper gas may meet part of the future gap. Extended use of oil—a notable present trend in the home—further aggravates supply difficulties and could hardly be welcomed as a national policy. Solid smokeless fuels have an advantage over oil in requiring no special storage facilities. Nonetheless their use must probably be regarded as ephemeral.

There remains the question of the value of coal and oil for chemical and related purposes. By-products of coal carbonization such as pitch, benzene, naphthalene and tar acids are likely to fall short of demand in the future. Lubricants represent a by no means negligible fraction of oil consumption and cannot be replaced by nuclear energy. There will also remain a need for other chemicals such as plastics and detergents, and for chemical reducing agents including coke—all uses where the carbonaceous nature of coal or oil is an essential feature. In the U.K. the individual tar chemicals mentioned may only amount to half a million tons per annum even in 1975, though one million tons of pitch should perhaps also be included in the essential category. Annual consumption of lubricants now amounts to over a million tons, that of plastics and detergents to over half a million tons; and that of coals used in coke ovens may rise to over 40 million tons per annum by 1975. The sum total in tons of carbon must give rise to serious thought regarding the use of the world's remaining oil resources now and those of coal before long. Professor HUGH NICOL has even questioned how far food supplies are dependent on carbonaceous fuel. This, however, is by no means self-evident.

To sum up. The projection of total energy demands to 1975 is fraught with uncertainty. In the U.K. this ought to be reflected chiefly in demand for oil which may be little more than at present, or 50 to 80 million, or even as much as 150 million tons a year coal equivalent. In the U.S.A. at that time coal requirements may lie between 400 million long tons and double that amount, those of oil and natural gas between 900 and 1 500 million tons a year coal equivalent. In this country generation of electricity from coal makes the least demand on capital resources but generation from nuclear energy is essential if industry expands, though not yet competitive; means

* *Coke & Gas* 18 (No. 209) (1956) 405.

must be found for enabling the latter to carry part of the peak load after 1971–72. Oil for the production of electricity has the disadvantage of high total capital investment and uncertainty of supply. It is essential to help coal to meet the competition of oil over the next 20 years lest coal-producing capacity, later needed, be lost. Conversion of coal to oil is a technically attractive means to this end but costs, especially the capital required, need to be greatly reduced.

The political problem of access to oil is likely to grow more acute and an ultimate crisis in supplies may occur after the middle of the next century, by which time, though coal should last hundreds of years, its adequate production in the U.K. may also present problems. Some part of carbonaceous fuels should be reserved for uses in which the carbon content, as distinct from the fuel value, is important, e.g. the manufacture of lubricants and chemicals. If a portion of the oil resources is to be thus reserved, a world agreement on its allocation—a vain hope?—will be needed before the end of this century; in the U.K., plans for the use of coal should shortly take this factor into account. The supply of good coking coals should be secure in both the U.K. and U.S.A. until towards the end of this century, beyond which there is no sound basis for prediction; but America has adequate supplies of lower-grade coking coals. In this country cheap smokeless fuels may soon present a problem, and use of solid fuels in the home may prove ephemeral.

Many of the problems that emerge from this attempt at crystal gazing are of an economic or engineering nature unsuited to the pages of *Fuel*, but papers describing improvements in or even novel methods of converting coal to oil may be expected. Whether or not the constitution of coal will be relevant to this and to what extent it will continue to be studied cannot be foreseen. Undoubtedly, however, some chemical conversions of coal—why not of oil also?—will be described, and more detailed chemical examinations of the coal carbonization process in all its aspects will be presented. The reactivity of carbonaceous fuels may receive some attention. There may also be special scientific aspects of nuclear energy production best suited to a journal of this type. The science of rocket fuels is an appropriate subject, though here there may be overlap with the sister Journal, *Combustion and Flame*. Studies of peat, brown coal and lignite have not in the past received much prominence in *Fuel* but this situation may be remedied. An invitation is extended to those working in all the above and similar fields to consider *Fuel* as a possible medium of publication.

The volume for 1958 has continued the main themes of recent years almost unchanged: coal analysis, coal constitution and physical properties, and mineral matter. One paper was concerned with binders for carbon electrodes and more attention might well be given to carbon products other than coke.

The continuing support of Dr C. H. Ruof as Deputy Editor (U.S.A.), the Overseas Correspondents, the Editorial Committee, and of Dr Kirkby with his invaluable *Notes*, and the help rendered by the referees, are gratefully acknowledged. And the unremitting labours of the publishers should not pass without due appreciation.

H. G. B. Dyden

Hydrogenation Products from Bituminous Coal and Sucrose at Elevated Temperatures; Spectral Comparisons

M. G. PELIPETZ* and R. A. FRIEDEL*

Nearly identical products were obtained by similar hydrogen treatments of bituminous coal and sucrose. Quantitative product distributions are compared. Infra-red, ultra-violet, and mass spectra show the chemical similarity of the asphaltenes and oils obtained; differences are confined to variations in concentrations of the constituents. Analyses of the 450°C light oils from sucrose and coal show parallel concentrations of naphthenes, paraffins, aromatics and phenols. The spectral comparisons provide further evidence of the coal-like character of pyrolysis products of carbohydrates. The production of aromatics from sucrose supports the finding of benzenes in products from the thermal treatment of carbohydrates.

THE present paper is a report on the similarity of the products obtained from hydrogenating coal and sucrose. Various workers have found that material similar to coal or coal products can be prepared from carbohydrates by various treatments, including hydrogenation[1-13]. The criteria of similarity generally have been ultimate analyses and brief investigations of the products, although the recent work of J. J. T. M. GEERARDS *et al.* reported various physical constants and *n–d–M* determinations[13]. In our attempt to compare chemical constitutions of the products from hydrogenation of coal and sucrose, infra-red (i.r.), ultra-violet (u.v.), and mass spectra have been determined. Aromatic compounds in the sucrose product have been studied and compared with aromatics in the coal products. M. BERTHELOT has shown that benzene is produced by hydriodic acid reduction of carbohydrates[1], and R. C. SMITH and H. C. HOWARD have demonstrated the existence of benzene rings in cellulose chars[12].

Previous investigations of coal hydrogenation in this laboratory have been published[14-17]. Previous publications on i.r. spectra have demonstrated the similarity of the spectra of coal, carbohydrate chars, and asphaltenes from coal and petroleum[18, 19]. Ultra-violet and visible spectra of coal and coal products have also been studied[20].

EXPERIMENTAL

Powdered Pittsburgh seam coal and sucrose were hydrogenated in batch autoclaves at 400° and 450°C for one hour in the presence of 1 per cent tin and 0·5 per cent ammonium chloride under 2 500 lb/in² initial (room temperature) hydrogen pressure. Experimental procedure and calculations have been reported[14, 16]. The charge in each experiment was 50 g of either coal or sucrose, 0·5 g powdered tin, 0·25 g ammonium chloride, and about

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15 g hydrogen. The detailed analyses of gaseous hydrocarbons were made on samples from runs at 400°C, 4 000 lb/in² hydrogen pressure, and 1 per cent molybdenum. The hydrocarbons were analysed by mass spectrometer in the presence of about 99 per cent hydrogen.

The i.r. spectra of the light oils were determined in 0·1 mm sealed cells; the heavy oils were examined in 0·038 mm demountable cells. The spectra of the asphaltenes were determined on films prepared in a stainless steel press by melting asphaltene between rock salt windows separated by 0·038 mm spacers. Asphaltenes from sucrose were more difficult to cast into films and did not transmit i.r. radiation as well as did the asphaltenes from coal.

Definitions

Asphaltene is defined as material that is benzene soluble-hexane insoluble[17]. Oil is the hexane-soluble material; light oil is the portion of oil distillable at 105°C and 3 mm pressure, and heavy oil is the residue from this distillation.

CHEMICAL DATA

The products given in *Table 1* illustrate the parallel behaviour of coal and sucrose under hydrogenation at 400° and 450°C. The hydrogen consumption for both coal and sucrose at 400°C was about 10 per cent of the original

Table 1. Distribution of products obtained from hydrogenating sucrose and bituminous coal

Initial hydrogen pressure, 2 500 lb/in²; 1 per cent tin; hydrogenation for 1 hour; 50 g charge

Hydrogenation run	*Sucrose*		*Coal*	
	400°C	450°C	400°C	450°C
Products, g				
Benzene insolubles	2·4	0·5	12·5	7·3
Asphaltene	9·4	1·0	30·2	10·0
Oil	5·6	14·4	4·2	25·4
Heavy	~4·4	~11·2	~3·1	~19·0
Light	~1·2	~ 3·2	~1·1	~ 6·4
Gaseous hydrocarbons	4·0	6·3	1·7	5·6
Alcohols	0·70	0·70	*Trace*	0·01
Water	22·0	23·2	2·5	3·2
Carbon dioxide	7·0	6·4	0·2	0·1
Total	51·1	52·5	51·3	51·6
Hydrogen absorbed (approx.)	1·4	2·1	1·3	2·3

hydrogen charge; at 450°C hydrogen consumption for both was about 15 per cent. At 400°C the principal carbonaceous product from both sucrose and coal was asphaltene; at 450°C it was oil.

The ultimate analyses of the products from sucrose and coal correspond to analyses reported in previous hydrogenations of coal and of carbohydrates[1-11, 17]; analyses of the benzene insolubles, asphaltenes and heavy

oils are given in *Table 2*. The asphaltenes produced at 400°C from both coal[16] and sucrose contained more hydrogen than the corresponding ones produced at 450°C. Asphaltenes produced from sucrose at 400°C contained more oxygen than those from coal; this result is also indicated by the appearance of aliphatic carbonyl bands in the i.r. spectra of the sucrose asphaltenes.

Table 2. Ultimate composition (weight per cent) of asphaltenes and heavy oils from hydrogenation of sucrose and bituminous coal

Component	*Benzene insolubles*				
	H	C	N	S	O
Sucrose, 400°C	4·1	71·3			24·6
Sucrose, 450°C	—	—			
Coal, 400°C	5·4	83·5	1·5	(3·6)	(6·0)
Coal, 450°C	4·1	78·7	1·8	(5·6)	(9·8)

Component	*Asphaltenes*				
	H	C	N	S	O
Sucrose, 400°C	7·2	86·2			6·6
Sucrose, 450°C	6·3	89·5			4·2
Coal, 400°C	7.7	87·4	1·2	0·3	3·4
Coal, 450°C	6·4	89·1	1·2	0·3	3·0

Component	*Heavy oils*				
	H	C	N	S	O
Sucrose, 400°C	9·3	88·4			2·3
Sucrose, 450°C	8·8	89·4			1·8
Coal, 400°C	8·5	89·0	0·7	0·2	1·6
Coal, 450°C	8·7	89·3	0·5	0·1	1·4

SPECTRAL DATA

Asphaltenes—The i.r. spectra of the asphaltenes, *Figure 1*, show the similarity of the basic chemical structures obtained in both sucrose and coal asphaltenes. Differences in molecular weight or polymer size would not produce large differences in the i.r. spectra. The asphaltene spectra also resemble the spectrum of Pittsburgh seam vitrain[18, 19].

The spectra of asphaltenes from sucrose and coal hydrogenated at 400°C are similar but have fewer absorption bands than those of the asphaltenes obtained at 450°C. The sucrose products at both temperatures show carbonyl bands at 5·85 microns that the coal products do not possess. The spectrum of asphaltene from sucrose hydrogenated at 400°C shows a higher hydroxyl content at 3·0 microns than that of the 400° coal asphaltene; but the 450° asphaltene spectra have identical 3·0 micron bands. The spectra of coal

asphaltenes differ slightly from the corresponding spectra of sucrose asphaltenes in the 8·5 micron region.

Heavy oils—The i.r. spectra of the heavy oils from sucrose and coal (*Figure 2*) are even more similar than those of the asphaltenes. A trace of carbonyl compounds is indicated in the 400°C-sucrose heavy oil, but none can be seen in the spectrum for the 450°C-sucrose product. Both spectra exhibit slightly more hydroxyl content (higher in the 400°C sample) than those from coal. All four spectra have the same bands from 6 to 15 microns.

The u.v. spectra of the heavy oils are also virtually the same (*Figure 3*).

Light oils—The mass spectra (*Figure 4*) of light oils obtained from sucrose and coal hydrogenated at 450°C show the same mass peaks. Peaks for aromatics, hydroaromatics, phenols, naphthenes and paraffins can be distinguished. Type analyses of these oils are compared in *Table 3*. The

Table 3. Comparison of composition of light oils from 450°C hydrogenation of sucrose and bituminous coal; mass spectral type analyses

Component	*Sucrose*	*Coal*
	volume per cent	
Naphthenes	56·	56·
Paraffins	27·	18·
Aromatics	15·	21·
Benzene	1·	1·
Toluene	3·	4·
C_8 *Alkylbenzenes*	6·	9·
C_9 *Alkylbenzenes*	3·	5·
C_{10} *Alkylbenzenes*	1·	1·
Tetralin and/or methylindans	0·3	0·7
Naphthalene	0·2	0·5
*Phenols and aromatic ethers**	2·	5·

* Combined mass, i.r. and u.v. data.

aromatic content of the coal product is greater. Phenol and C_7 and C_8 phenols and/or aromatic ethers are indicated in both spectra; the phenolic content of the coal product is somewhat higher. The naphthene contents are identical; the paraffin content in the sucrose product is higher. Small amounts of naphthalene and tetralin and/or methylindans are indicated in the spectrum of the light oil from coal; smaller amounts are indicated in the spectrum of the sucrose light oil.

The i.r. spectra of these products are complex, but the same bands occur in both. The higher phenolic content of the coal product noted in the mass spectra is shown here by stronger absorption at 3·0 and 8·0 microns and at some of the long wavelength bands (*Figure 5*). All bands appear to support the mass spectral evidence that the major components are the same.

The u.v. spectra are apparently composites of the spectra of aromatic hydrocarbons, phenols and other components (*Figure 6*). The spectral intensities for the light oil from coal are greater than those of the light oil from sucrose.

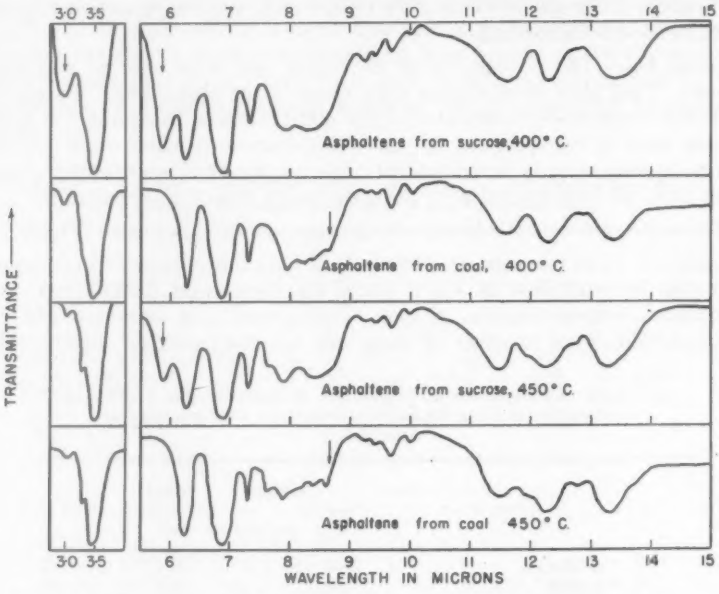
3·0 3·5
6 7 8 9 10 11 12 13 14 15
Asphaltene from sucrose,400° C.
Asphaltene from coal, 400° C.
Asphaltene from sucrose, 450° C.
Asphaltene from coal 450° C.
TRANSMITTANCE
WAVELENGTH IN MICRONS

Figure 1. Infra-red spectra of asphaltenes from hydrogenation of coal and sucrose; arrows indicate spectral differences (by courtesy of U.S. Bureau of Mines)

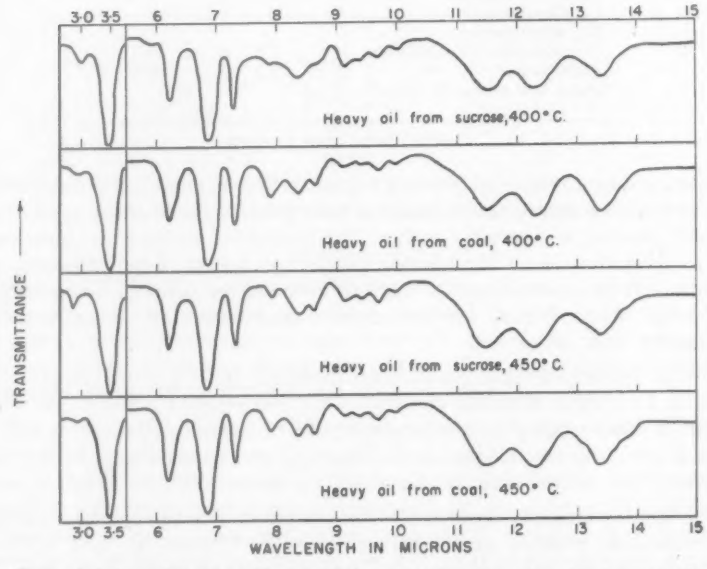
3·0 3·5
6 7 8 9 10 11 12 13 14 15
Heavy oil from sucrose,400° C.
Heavy oil from coal, 400° C.
Heavy oil from sucrose, 450° C.
Heavy oil from coal, 450° C.
TRANSMITTANCE
WAVELENGTH IN MICRONS

Figure 2. Infra-red spectra of heavy oils from hydrogenation of coal and sucrose (by courtesy of U.S. Bureau of Mines)

LOG PEAK HEIGHT

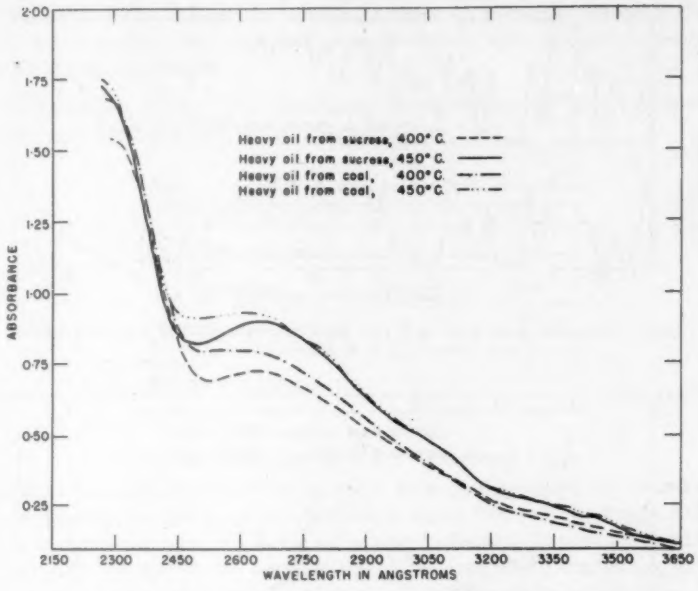

Figure 3. Ultra-violet spectra of heavy oils; 1 cm cell, about 0·02 g/l. in cyclo*hexane (by courtesy of U.S. Bureau of Mines)*

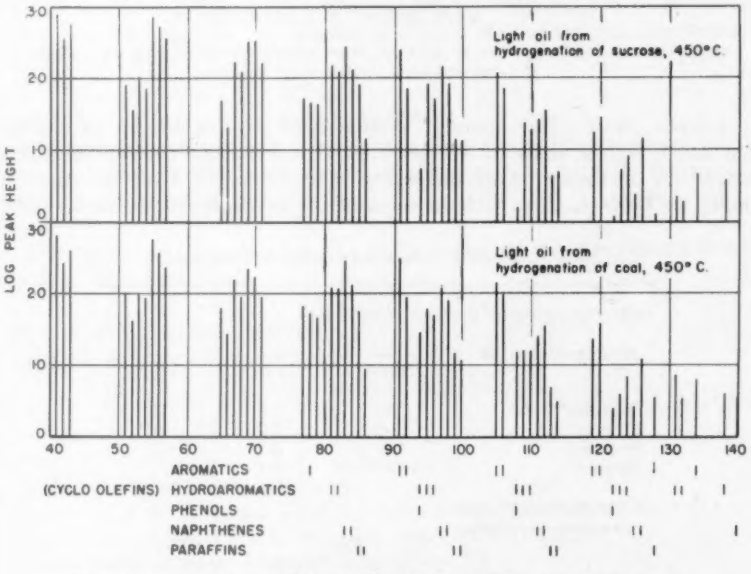

Figure 4. Mass spectra of light oils from hydrogenation of coal and sucrose (by courtesy of U.S. Bureau of Mines)

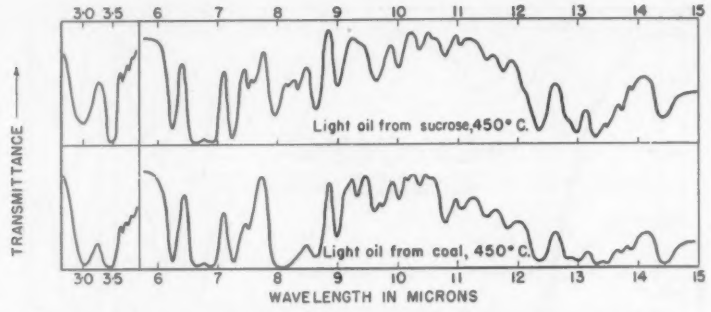

Figure 5. Infra-red spectra of light oils from hydrogenation of coal and sucrose (by courtesy of U.S. Bureau of Mines)

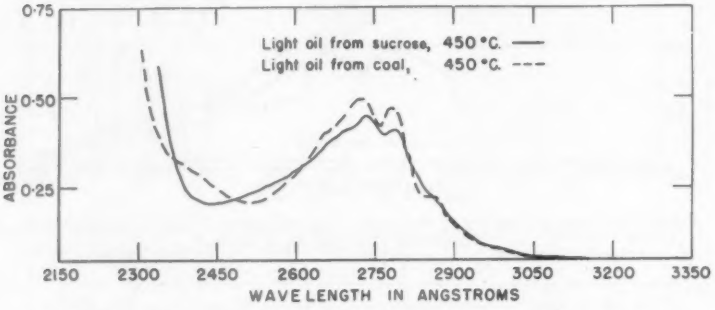

Figure 6. Ultra-violet spectra of light oils from hydrogenation of coal and sucrose (by courtesy of U.S. Bureau of Mines)

Aqueous phase—The aqueous phases from hydrogenation of sucrose contained higher amounts of alcohols. These concentrations decreased, except for methanol, with increasing temperature of hydrogenation, as shown in *Table 4*. Ultra-violet spectra of the aqueous phases from sucrose

Table 4. Analyses (volume per cent) of aqueous phases

Mass spectrometer analysis of alcohols:	*Sucrose*		*Coal*
Hydrogenation run	400°C	450°C	450°C
Methanol	0·1	0·9	0·1
Ethanol	3·0	2·2	0·2
Propanols	0·8	0·5	
Butanols	0·2	0·1	
Ultra-violet qualitative analysis of phenols:	*Phenol* o- *or* m-*Phenols* p-*Phenols*		*Phenol* o- *or* m-*Phenols* p-*Phenols*

and coal at 450°C demonstrated the presence of phenolic mixtures. Phenol and *ortho*- and/or *meta*-phenols predominated, with smaller amounts of *para*-phenols also present.

Hydrocarbon gases—The analogous compositions of the hydrocarbon gases from sucrose and coal are given in ***Table 5.***

Table 5. Composition (volume per cent) of gaseous hydrocarbons from hydrogenation of sucrose and coal at 400°C, 4 000 lb/in² hydrogen, 1 per cent molybdenum

Component	*Sucrose*	*Coal*
Methane	61·	57·
Ethane	19·	23·
Propane	13·	13·
Butanes and higher	7·	7·

HYDROGENATION OF A 250°C SUCROSE CHAR

Sucrose char prepared at 250°C has also been hydrogenated for the purpose of comparing the products obtained with those from the hydrogenation of sucrose. In the heating of a batch autoclave containing sucrose and hydrogen up to 400° or 450°C the sucrose might be completely converted to char before any appreciable hydrogenation occurs. The hydrogenation products from sucrose and the 250°-sucrose char would thus be identical. However, a preliminary investigation of the products from the char hydrogenation shows a greater yield of insoluble material than is obtained from sucrose. This may indicate an appreciable reactivity for sucrose at temperatures below 250°C.

CONCLUSIONS

The resemblance of product compositions from the hydrogenation of sucrose and coal provides further evidence of the coal-like character of pyrolysis products of carbohydrates.

This paper was presented at the fall meeting of the American Chemical Society, New York, 1951.

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(*Received December 1957*)

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*Chemical Structure and Properties of Coal XXI—The Kinetics of Coal Carbonization**

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Earlier studies of the kinetics of coal carbonization, in which the change in weight is used as a parameter for following the reaction, are considered and shown to give information concerned mainly with the evolution of tar, so that other methods are needed for the study of the kinetics of the evolution of the remainder of the volatile material. The method adopted is the determination of the flow rate of each of the gases concerned under a vacuum at rising temperature by measuring the flow rates of all the gases, and frequent gas analysis. The vitrinites of a series of coals varying in rank from anthracite to a high volatile coal and the other macerals of one of these coals are examined. Experimental results for flow of hydrogen, methane, the other hydrocarbons, carbon monoxide and the rate of weight loss for some of the coals are shown. It is found that coals containing about 92 per cent carbon give the greatest total amount of hydrogen, while the most methane is found in coals of 89 per cent carbon. The maximum of the other hydrocarbons is found in coals of about 86 per cent carbon. Methane flow takes place as a first order reaction up to about 500°C. Thereafter, the flow becomes larger than expected, which is interpreted in terms of the self-hydrogenation of the coal, for which independent evidence is also advanced. Hydrogen flow also takes place according to the first order up to about 500° to 550°C. Then the flow becomes less than expected, which is interpreted as showing that the activation energy of this reaction increases beyond these temperatures, owing to the structural changes now taking place in the coke. Making the assumption that the tar obtained in vacuum pyrolysis represents that portion of the coal but lightly (or not at all) bonded to the remainder, a value for the mean lamellar diameter for each coal is found, which is in good agreement with other published data.

IN the study of the kinetics of a chemical reaction its progress is usually followed by measuring the changes in some parameter during the course of the reaction, the relationship between the value of the chosen parameter and the concentration (i.e. the number of molecules present) of reactant being determined separately.

In earlier studies of carbonization kinetics[1–3] the parameter used to follow the reactions was the loss of weight, the material volatilized being treated as the product of the reaction. As the nature of the products of the reaction changes in the course of the reaction from tars having high molecular weights to almost entirely hydrogen, the change of weight is not a suitable parameter to characterize the *overall* reaction. In the early stages of carbonization the tar is contributing most to the change in weight, so that the gravimetric studies referred to are mainly concerned with the evolution of tar from coal. With this restriction and the assumption that the molecular weight of the tar is approximately constant the kinetics are acceptable. Beyond about 500°C van Krevelen and co-workers and Boyer find it necessary to postulate 'secondary degasification', to account for the discrepancy between the observed change in weight, and what the simple theory used by them predicts.

* A fuller treatment of this work will be found in *Communication 516* of the Institution of Gas Engineers (November, 1957) of the same title. The present paper contains modifications not given in *Communication 516*.

Table 1

Reference letter	N.C.B. Coal Rank Code No.	Origin of coal		Proximate analysis %			Ultimate analysis d.a.f. %					Atomic ratios		Petrographic analysis %		
		Mine	Seam	VM d.a.f.	Dry basis ash	Air dry moisture	C	H	O	N	S	H/C	O/C	Vitrinite	Exinite	Fusinite and micrinite
A	100b	*Jacoba-Sophia*	*Not known*	8·2	1·7	2·1	93·7	3·5	1·0	1·4	0·7	0·45	0·008	100	0	0
H	201b	*Hendrik*	*XVIII*	13·7	0·8	1·2	91·7	4·1	1·9	1·9	0·9	0·54	0·016	81	0	19
E	301	*Emma*	*III/IV*	23·3	3·7	1·0	88·6	5·0	3·7	2·3	0·8	0·68	0·031	92	2	6
M	401a	*Maurits*	*D*	30·6	4·8	1·6	86·8	5·3	4·7	2·0	1·3	0·73	0·041	78	6	16
Bv	6/701	(*Vitrinite*)	*Beeston,*	35·7	1·1	7·1	83·7	5·2	8·5	1·9	0·9	0·75	0·076	95	2	2 1
Be	402	(*Exinite*)	*West*	63·5	1·1	2·6	84·6	6·7	6·8	1·4	1·0	0·95	0·060	0	95	0 5
Bm	901	(*Micrinite*)	*Yorks*	26·5	6·3	3·9	86·2	4·3	8·1	1·4	0·8	0·60	0·070	0	13	0 87
F	802	*Faulquemont*	*Not known*	41·9	2·0	6·2	80·2	4·9	13·4	1·2	0·6	0·73	0·125	98	1	1 0

NOTE: For coals A, H, E, M and F the analyses refer to the samples as actually used, while for the macerals of coal B, the analyses refer to the pure macerals, corrections for the contents of other macerals having been made.

In the present work these difficulties are overcome by considering each molecular species separately in applying kinetic theory. This enables far-reaching conclusions to be drawn concerning the nature of the carbonization reactions and coal structure.

EXPERIMENTAL

The work was carried out by pyrolysing 3 g samples of the vitrinites listed in *Table 1* at a pressure of between 10 and 20 mm of mercury in a silica tube within a steel block furnace of large thermal capacity, which allowed linear heating rates to be achieved easily. Moisture and tar condensed in an ice trap, and the volume flow rate of the remaining gases was measured, using a method not influenced by the fact that the composition of the gas was changing. Small gas samples were taken frequently and analysed by gas chromatography giving the concentrations of hydrogen, methane, hydrocarbons (individually) up to C_4, and the oxides of carbon. It was thus possible to draw graphs relating the flow rates of each of these gases to temperature. The heating rate used was 1·8°C/min, this rather low rate being chosen to give sufficient time in the specially interesting early stages of the reaction to carry out the various manipulations required in taking a maximum number of samples. Some experiments were done at 0·9 and 3·6°C/min, but this had no influence on the flow rates observed (expressed in terms of cm³/°C) and on the totals of the various gases. Owing to practical difficulties the reproducibility of the fast experiments was poor. The temperature limit of all experiments

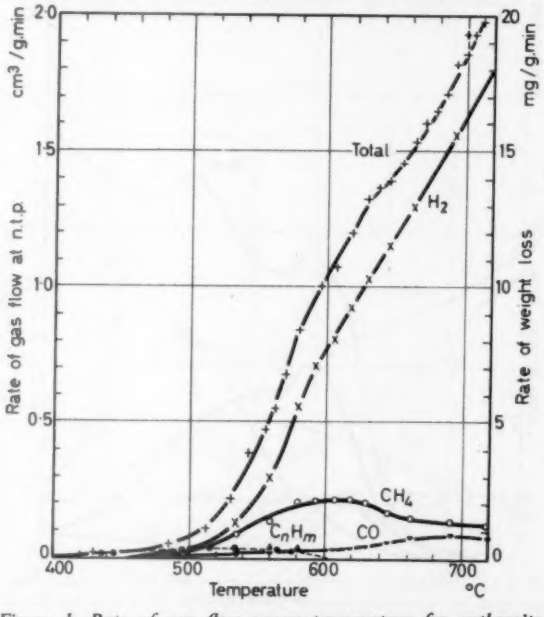


Figure 1. Rate of gas flow versus temperature for anthracite A at 1·8°C/min. Dashed line represents rate of weight loss against temperature, referring to right-hand ordinate

was at about 730°C, as the steel of the furnace block undergoes a structural change at this temperature, resulting in a temperature arrest, so that the linear heating programme could not be maintained.

RESULTS

Figures 1 to *5* show the gas flow against temperature curves for the anthracite A, the vitrinite of the coking coal E, and the vitrinite, exinite and micrinite of the high volatile coal B. The vitrinites intermediate in rank have curves falling between the ones shown, while that of the vitrinite of highest volatile matter, F, shows no new features, so that these are not reproduced.

The flow rates of saturated hydrocarbons (other than methane) found for vitrinite of coking coal E are shown in *Figure 6*. It is interesting to note that all show the maximum flow at the same temperature, some 30°C lower than the temperature of maximum methane flow. *Figure 7* shows the flow of unsaturated hydrocarbons from the vitrinite of coking coal E.

Figure 8 shows the unsaturated hydrocarbons obtained from the exinite Be which is unexpected in that ethylene is not the most important component, the maxima of both butylene and propylene being higher. *Figure 9* shows the saturated hydrocarbons obtained from the exinite Be.

Very small amounts of carbon dioxide are found. There are usually two peaks, as shown in *Figure 10*. These may correspond to the two types of carboxyl groups identified by Blom on the basis of chemical reactivity (private communication).

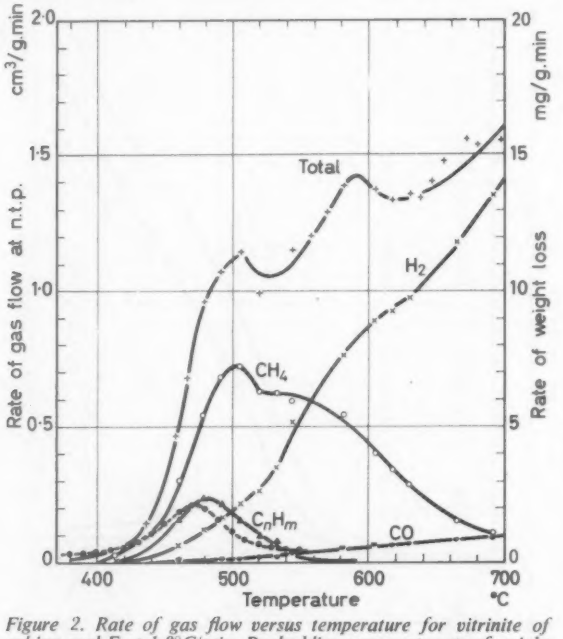


Figure 2. Rate of gas flow versus temperature for vitrinite of coking coal E at 1·8°C/min. Dashed line represents rate of weight loss against temperature, referring to right-hand ordinate

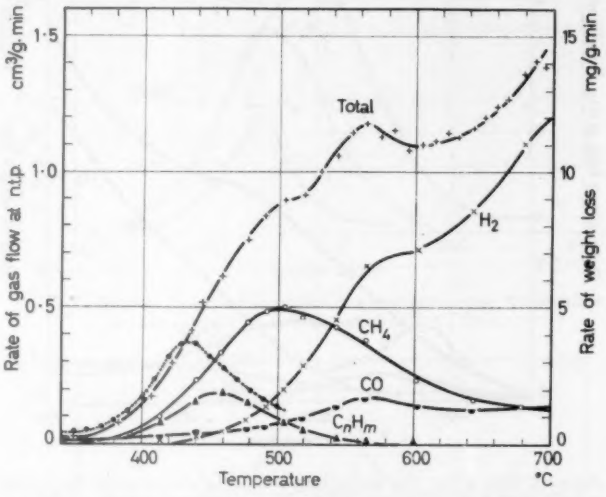


Figure 3. Rate of gas flow versus temperature for the vitrinite Bv of high volatile coal B at 1·8°C/min. Dashed line represents rate of weight loss against temperature, referring to right-hand ordinate

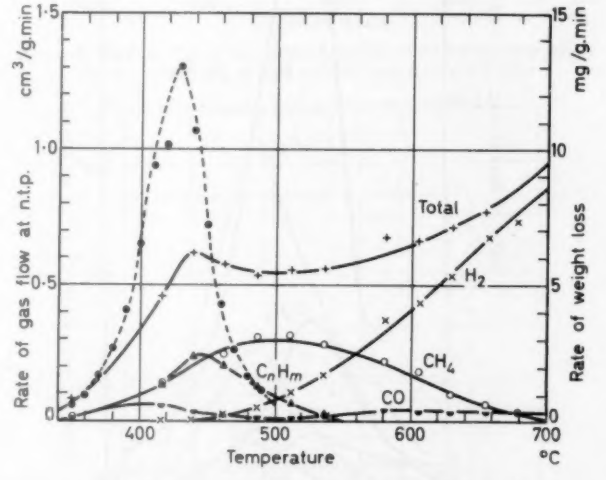


Figure 4. Rate of gas flow versus temperature for the exinite Be of high volatile coal B at 1·8°C/min. Dashed line represents rate of weight loss against temperature, referring to right-hand ordinate. Note double maxima in CO flow

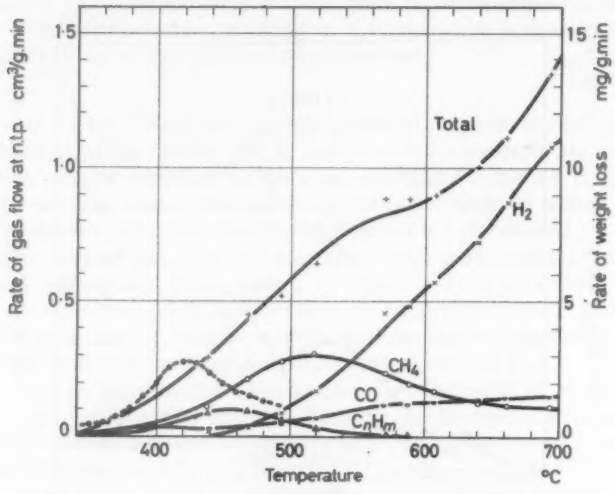


Figure 5. Rate of gas flow versus temperature for the micrinite Bm of high volatile coal B at 1·8°C/min. Dashed line represents rate of weight loss, referring to right-hand ordinate

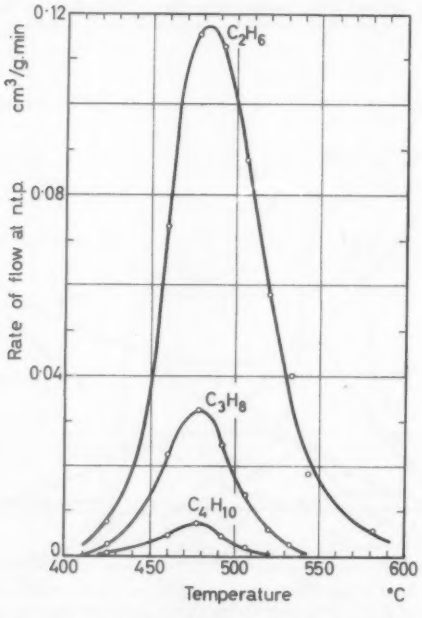


Figure 6. Rates of flow of saturated hydrocarbons versus temperature for the vitrinite of coking coal E at 1·8°C/min

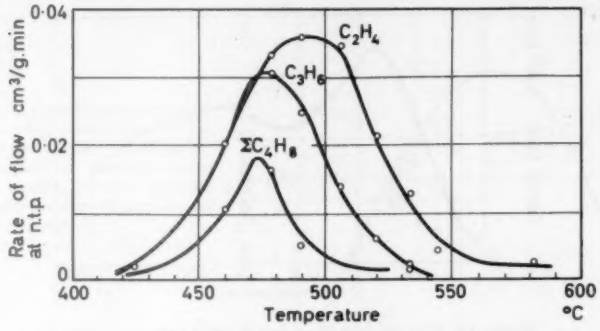


Figure 7. Rates of flow of unsaturated hydrocarbons versus temperature for the vitrinite of coking coal E at 1·8°C/min

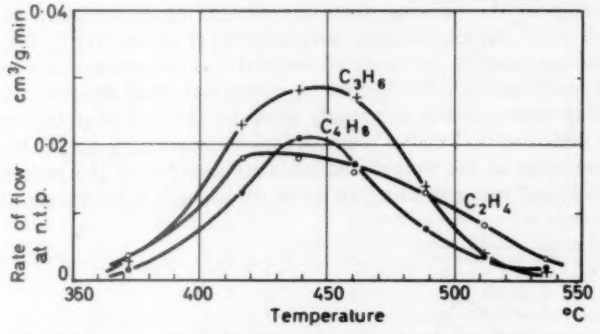


Figure 8. Rates of flow of unsaturated hydrocarbons versus temperature for the exinite Be of high volatile coal B at 1·8°C/min

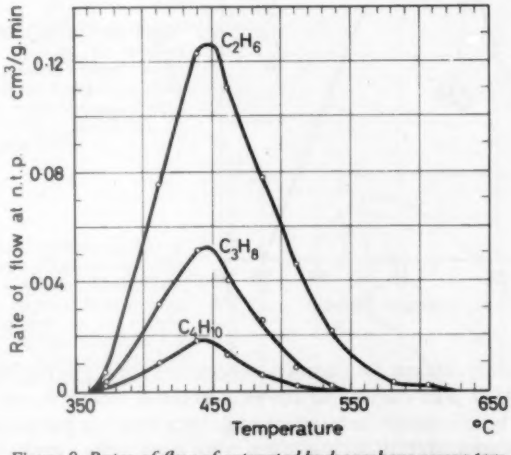


Figure 9. Rates of flow of saturated hydrocarbons versus temperature for the exinite Be of high volatile coal B at 1·8°C/min

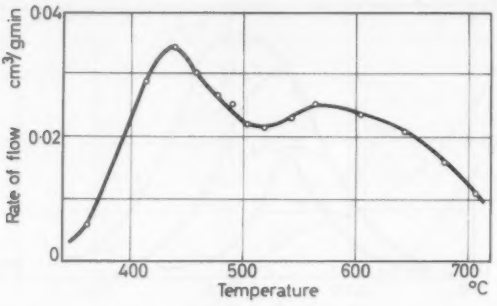


Figure 10. Rate of flow of carbon dioxide versus temperature for vitrinite Bv of high volatile coal B at 1·8°C/min

The totals of the various gases are plotted against carbon content in *Figures 11* to *16*. As experiments were stopped at about 700°C, the amounts of the various gases to be expected beyond this temperature are estimated. For methane (*Figure 11*) this is done by extrapolation of the flow rate against temperature curve, which is already close to zero, so that the amount of methane added to that above is small. For hydrogen (*Figure 12*) this is done by a knowledge of the weight and ultimate analysis of the residue, all the hydrogen found being assumed to come off as such if the temperature were

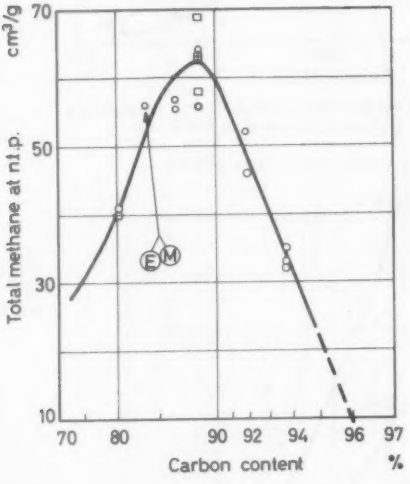


Figure 11. Total methane (extrapolated to end of reaction) versus carbon content. Arrows show associated vitrinite of the exinite and micrinite examined.
○ 1·8°C/min; □ 3·6°C/min; + 0·9°C/min

raised sufficiently, except the quantity needed to supply the methane estimated by extrapolation. The curve also shows a point at about 96 per cent carbon which gives the maximum amount of hydrogen which a particular anthracite could have produced if all its hydrogen were given off as such. This confirms the position of the maximum at about 92 per cent carbon. For carbon

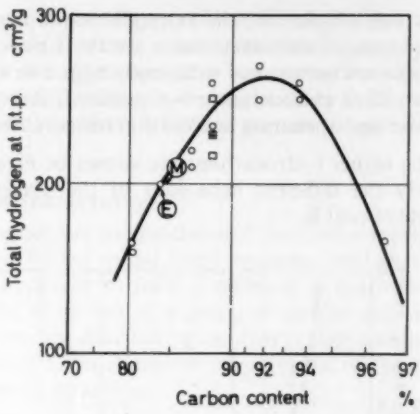


Figure 12. Total hydrogen (extrapolated to high temperatures from analysis of residue, allowing for methane not yet evolved) versus carbon content. Arrows indicate associated vitrinite of exinite and micrinite examined. ○ 1·8°C/min; □ 3·6°C/min; + 0·9°C/min

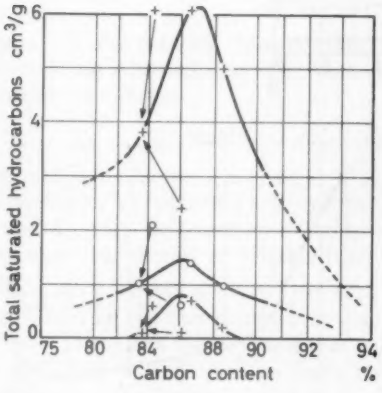


Figure 13. Total saturated hydrocarbons versus carbon content. Top curve: C_2H_6; middle: C_3H_8; bottom: C_4H_{10}. Arrows indicate the associated vitrinite of the exinite (at about 85% C) and micrinite (at about 86% C) examined. Dashed curves are estimated

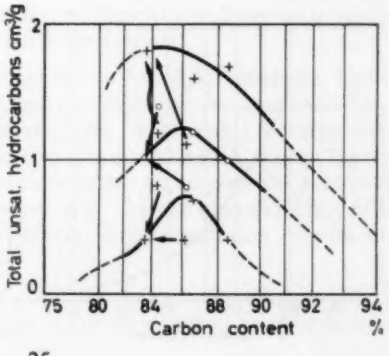


Figure 14. Total unsaturated hydrocarbons versus carbon content. Top curve: C_2H_4; middle: C_3H_6; bottom: C_4H_8. Arrows indicate the associated vitrinite of the exinite (at about 85% C) and micrinite (at about 86% C) examined. Dashed curves are estimated

monoxide (*Figure 16*) the extrapolation is made on the assumption that all the oxygen of the coke residue would come off as carbon monoxide, if the temperature were raised sufficiently high. For reasons given below the carbon monoxide is considered in two portions, that appearing up to 500°C (*Figure 15*) and that appearing beyond that temperature.

The higher hydrocarbons are shown in *Figures 13* and *14* which indicate clearly the different behaviour of the macerals vitrinite, exinite and micrinite of coal B.

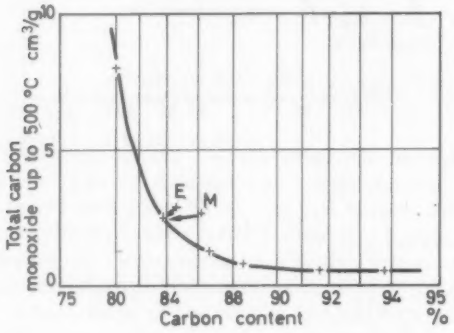
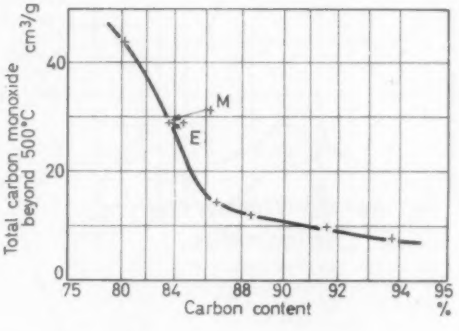


Figure 15. Total carbon monoxide up to 500°C versus carbon content. Arrows show associated vitrinite of the exinite and micrinite examined

Figure 16. Total carbon monoxide beyond 500°C (extrapolated to high temperatures from analysis of residue) versus carbon content. Arrows show associated vitrinite of the exinite and micrinite examined



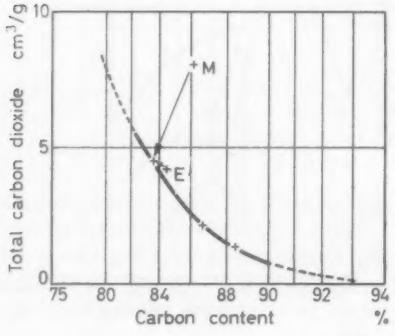


Figure 17. Total carbon dioxide versus carbon content. Arrows show associated vitrinite of the exinite and micrinite examined. The dashed curve is estimated

The most interesting observation on *Figure 17*, which shows the yield of carbon dioxide, is that the yield from the micrinite is much greater than that from vitrinite, even though its oxygen content is less. As carbon dioxide originates from carboxyl groups, and these can be produced by mild oxidation, this suggests that oxidation may have played a part in the genesis of micrinite.

INTERPRETATION

It is assumed that the various gases are the products of first order reactions in which the rate is determined by the initial bond breaking, and that the subsequent combination with hydrogen to form a molecule is much faster. If each type of bond is thought of as one of a group of similar oscillators sharing energy, then whatever the law distributing the energy, the number of oscillators having sufficient energy to break will be proportional to the number of bonds, which is the first order condition.

If v_0 is the total of volume of any one gas that can be produced and v is the volume produced up to a given instant, then

$$dv/dt = k(v_0 - v) \quad \ldots . [1]$$

where k is the reaction velocity constant. The temperature dependence of this constant is assumed to be given by the Arrhenius equation. Substituting this above we obtain

$$dv/dt = k_0(v_0 - v) \exp(-E/RT) \quad \ldots . [2]$$

where E is the activation energy, R is the gas constant, k_0 the frequency factor, and T the absolute temperature. The two unknowns in this relation, E and k_0, may be found by plotting $\ln (dv/dt)/(v_0 - v)$ against $1/T$, when a straight line should be produced having slope $-E/R$ and intercept $\ln k_0$.

This development assumes that each of the gases comes from the same origin. It is known that hydrogen in coal is present in aromatic, aliphatic and alicyclic forms, but it is assumed that only aromatic hydrogen will contribute to the gaseous hydrogen, as both the aliphatic and alicyclic hydrogen is bound to the lammellae via a C—C bond, which is normally weaker than any C—H bond[5], so that all aliphatic and alicyclic hydrogen will be removed in the form of hydrocarbons at lower temperatures. In the case of methane, the fact that a portion of the methane comes from an origin other than methyl groups becomes apparent in the analysis.

Figures 18, *19* and *20* give typical curves found for methane, hydrogen and carbon monoxide. *Figures 21* and *22* show how the activation energies observed for hydrogen and methane vary with rank, for temperatures below those at which the complications discussed below occur. There is a rising tendency with rank from values under 40 to over 60 kcal/mole as carbon content rises from 80 to 94 per cent. As the reproducibility of these measurements was not very satisfactory, little conclusion can be drawn from these figures.

In order to use equation 2 it is necessary to know v_0, though unless the reaction goes nearly to completion, it is not necessary to know it accurately.

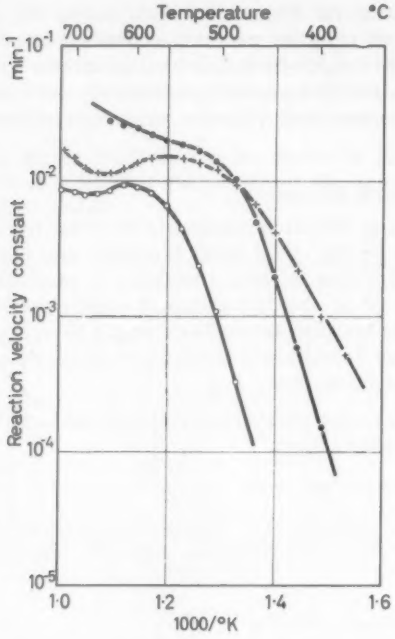


Figure 18. Arrhenius diagram for methane for anthracite A (○), vitrinite of coking coal E (●), and vitrinite Bv of high volatile coal B (+). The other coals examined fall between these according to rank

For methane the reaction is followed over a large part of its range so that v_0 can be determined from the volume of methane evolved, with an addition estimated from the extrapolated dv/dt against temperature curve. This is usually accurate to a few per cent, which is sufficient.

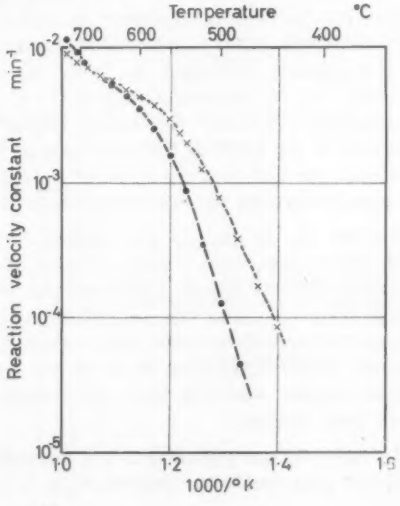


Figure 19. Arrhenius diagram for hydrogen from anthracite A (●) and vitrinite Bv of high volatile coal B (×). The other coals examined fall between these according to rank

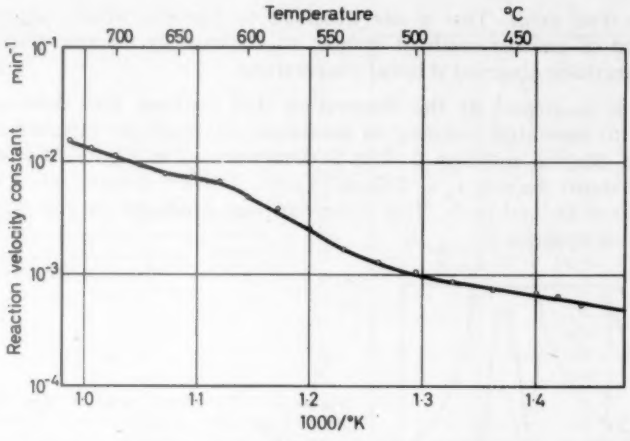


Figure 20. Arrhenius diagram for carbon monoxide for vitrinite from coking coal E

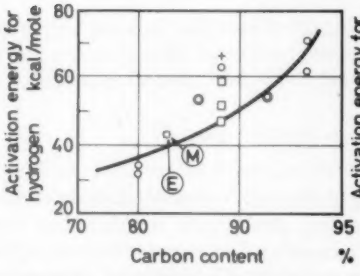


Figure 21. Activation energy versus carbon content for hydrogen. Arrows show the associated vitrinite of the exinite and micrinite examined. ○ 1·8°C/min; □ 3·6° C/min; + 0·9°C/min

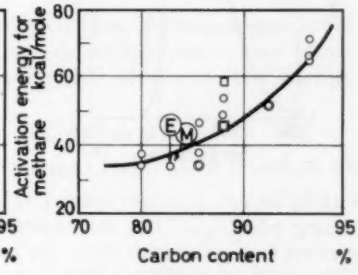


Figure 22. Activation energy versus carbon content for methane. Arrows show the associated vitrinite of the exinite and micrinite examined. ○ 1·8°C/min ; □ 3·6°C/min; + 0·9°C/min

v_0 for hydrogen is determined from the weight and analysis of the residue, it being assumed that all the hydrogen found will be given off as such, except for the small amount of methane still expected.

The Arrhenius diagrams for methane and hydrogen both show an initial steep part, followed by one of lesser slope, which may even become positive for methane. This means that the velocity constants of the reactions at higher temperatures are lower than the values at lower temperatures lead one to expect. For methane this happens when its flow rate is decreasing. Rewriting equation 1 as

$$k = (\mathrm{d}v/\mathrm{d}t)/(v_0 - v)$$

we see that k can only continue to increase while $\mathrm{d}v/\mathrm{d}t$ decreases if $(v_0 - v)$—the amount of methane which has not yet appeared—decreases even more

rapidly than dv/dt. This is not observed to happen, which suggests the existence of another methane source, in addition to the one responsible for the methane observed at lower temperatures.

This is confirmed by the observation that methane flow does not fall rapidly to zero after reaching its maximum, as would be expected from a reaction obeying equation 2. This is demonstrated in *Figure 23* where the full line shows the case $v_0 = 100\ cm^3$, $k_0 = 10^{15}\ min^{-1}$, heating rate 2°C/min, and $E = 46{\cdot}06$ kcal/mole. This curve has been produced by the numerical solution of equation 2.

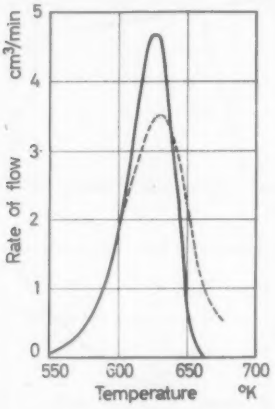


Figure 23. Calculated curve of flow rate versus temperature for the case $v_0 = 100\ cm^3$, $k = 10^{15}\ min^{-1}$, heating rate 2°C/min, and $E = 46{\cdot}06$ kcal/mole. Dashed curve shows effect of increasing E according to $E = 46{\cdot}06 + 0{\cdot}23\,(T - 600)$ for $T > 600°K$

With hydrogen, k is not increasing sufficiently quickly while dv/dt is still increasing and $(v_0 - v)$ is only decreasing slowly (the reaction not having progressed far), so that dv/dt is not increasing fast enough. It thus appears that an excess of methane occurs with a deficit of hydrogen at temperatures beyond about 500°C, which suggests that the reaction $C + 2H_2 = CH_4$ is taking place.

Independent evidence for this 'autohydrogenation' is provided by the work of F. J. DENT[4], who showed that methane may be produced from semicoke by high pressure hydrogen, in larger amounts than would be expected from the volatile matter of the semicoke. The threshold of the reaction is at about 400°C, and it accelerates rapidly after 500°C. Proof of the autohydrogenation reaction is provided by experiments carried out with nitrogen at one atmosphere and at fifty atmospheres. The methane yield in the former case may be taken as the yield from the volatile matter of the semicoke, and the considerable increase observed in the latter must be the result of 'autohydrogenation'. Experiments done at one atmosphere of hydrogen produce an amount of methane greater than that produced at one atmosphere of nitrogen by more than enough to account for the additional methane found in the experiments, so that the partial pressure of hydrogen inside the coal which is required to explain the excess methane need not be more than a fraction of one atmosphere, which may well be developed inside the microstructure of the coal. Dent's results are shown in *Figure 24*.

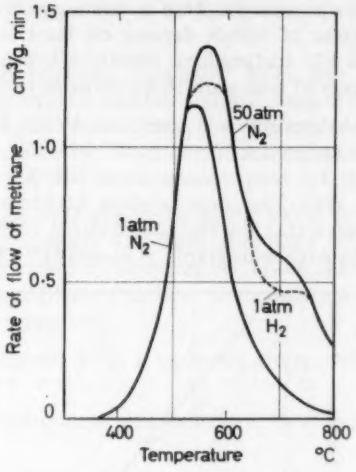


Figure 24. Rate of flow of methane versus temperature obtained from a semicoke under various atmospheres and pressures by F. J. DENT[4]

A further piece of evidence in favour of another methane source is the fact that all the saturated hydrocarbons except methane have their maximum flow at the same temperature, while that for methane is some 30°C higher.

THE COURSES OF THE REACTIONS

The course of the reaction for the production of methane is discussed above; the other major gases are considered below.

Carbon monoxide

Application of equation 2 leads to an activation energy curve which suggests that the carbon monoxide is the product of two or more reactions. This is also suggested by the long tail at the low temperature end of the flow/temperature graph, as if a flow of low activation energy is superimposed upon one of higher activation energy. This is clear in the case of the exinite Be, where a separate peak at about 400°C is clearly shown (*Figure 4*). In what follows, the first reaction will be supposed to produce all the carbon monoxide up to 500°C, while the second (and any other) will be credited with the rest.

Hydrogen

The autohydrogenation reaction by itself cannot explain the fact that at higher temperatures the hydrogen flow is less than expected from an extrapolation of that at lower temperatures. Even if all the methane after about 500°C were produced by autohydrogenation, the Arrhenius graph for hydrogen would still have a bend in it. The hydrogen flow is therefore still smaller at higher temperatures than would be expected from the flow at lower temperatures. The explanation offered for this is that owing to the structural changes taking place in the assembly of lamellae to which the hydrogen atoms are attached, surviving C—H bonds become stronger, and continue to become so with increasing temperature. This implies a steadily increasing

activation energy. This is not *a priori* impossible as it is known that the strengths of bonds depend on their surroundings. Thus, for example[5], it needs 101 kcal/mole to remove a hydrogen atom from a methane molecule, but only 87 kcal/mole to do the same with a free methyl group.

This hypothesis is confirmed by the dotted line on *Figure 23* which shows what happens to the curve of flow rate against temperature if the activation energy for temperatures above 600°K rises according to $E = 46{\cdot}06 + 0{\cdot}23\ (T - 600)$. The corresponding Arrhenius graph is given in *Figure 25* where it is shown that the rise in activation energy is accompanied by a fall in slope on the Arrhenius graph, as actually observed.

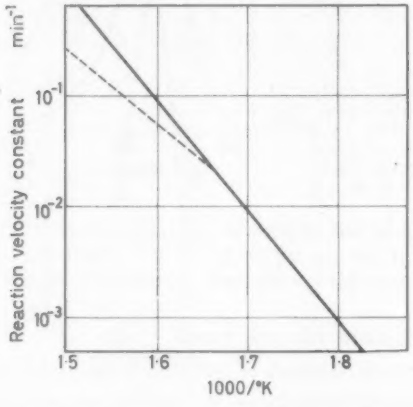


Figure 25. Arrhenius diagram corresponding to the calculated curves of Figure 23

H. A. G. CHERMIN and D. W. VAN KREVELEN[3] also find it necessary to suggest that the activation energy of coal carbonization increases with increasing temperature, basing this conclusion on gravimetric experiments. When there is no tar formation, these experiments are approximately comparable with those reported here.

THE STRUCTURE OF COAL

The results obtained, together with the following assumptions, some of which are controversial, enable a self-consistent picture of the structure of coal to be built up. The truth of the controversial assumptions is supported by the agreement between this and other methods of determining the mean size of coal lamellae.

(*1*) Coal consists of fully condensed aromatic lamellae of carbon atoms, with the edge valencies satisfied by various groups which form the volatile matter *other than tar*.

(*2*) The tar obtained under conditions of vacuum distillation is that part of the coal which is but weakly (or not at all) bonded to the remainder.

(*3*) The volatile matter, other than the tar, is formed as follows.

Hydrogen—Each hydrogen molecule originates from two peripheral sites, upon breaking of a C—H bond, followed by hydrogen molecule

formation. The molecule formation is assumed to be faster than the bond breaking process.

Hydrocarbons—Each hydrocarbon molecule originates from two peripheral sites, upon breaking of the appropriate carbon—radical bond, and the breaking of a C—H bond, followed by molecule formation. A portion of the methane is formed by autohydrogenation, for which the necessary hydrogen comes from four peripheral sites.

Carbon monoxide—The carbon monoxide appearing below 500°C is from carbonyl groups, occupying one peripheral site, and from ether links, occupying two sites. Carbon monoxide appearing at temperatures above 500°C is thought to be derived from oxygen replacing carbon in the periphery of lamellae, so that no peripheral sites are vacated.

Carbon dioxide—Carbon dioxide comes from a carboxyl group, without vacating a peripheral site.

Water—Water comes from hydroxyl groups and hydrogen, thus vacating two peripheral sites.

The calculation is done as follows. The carbon of the residue is assumed to be the aromatic carbon of the coal, with the exception of that part found in the tar, the portion removed by autohydrogenation, and the portion removed in the form of carbon monoxide above 500°C. These corrections are, however, small. The total number of peripheral sites of the lamellae in one gramme of coal is determined from the gas observed, as outlined above.

The atomic ratio C/H is now calculated, C being the number of aromatic carbon atoms and H being the number of radicals per gramme of coal. This ratio increases from unity as the number of rings per lamella increases, as shown in *Figure 26*. The upper curve applies to peri or complete condensation

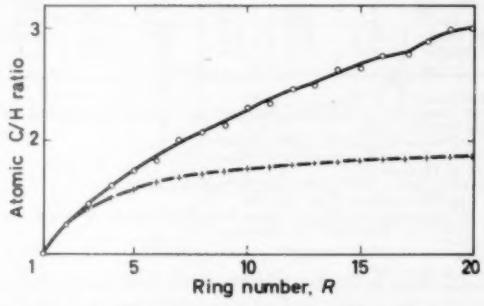


Figure 26. Relation between atomic C/H *ratio and ring number for fully condensed (upper curve) and cata condensed (lower curve) hydrocarbons*

and is used as a model in what follows, while the lower one applies to cata condensation, which gives a minimum to C/H for a given ring number R. For cata condensation C/H $\rightarrow$ 2 as $R \rightarrow \infty$. The lowest value of C/H observed is 1·9, the others being over 2, so that there is clearly a high degree of condensation.

Table 2 gives the results of applying these ideas to the data obtained. The rows in bold face type show how the ring number per mean lamella obtained by the method outlined agrees with those obtained by D. W. VAN KREVELEN and J. SCHUYER[6]. Except for exinite Be, the agreement is excellent. The upper part of *Table 2* gives the totals of the various products observed per gramme of coal carbonized, while the lower half gives the number of the different radicals per lamella.

Table 2

Coal	*Unit*	*A*	*H*	*E*	*M*	*Bv*	*Be*	*Bm*	*F*
Carbon content	%	93·7	91·7	88·6	86·8	83·7	84·6	86·2	80·2
*Coke residue**	mg/g	940	890	790	700	680	660	740	630
CH_4†	cm^3/g	33	49	62	57	56	33	34	41
H_2‡	cm^3/g	255	260	245	215	200	185	210	160
H_2O§	cm^3/g	0	12	38	50	60	56	56	87
CO *up to 500°C*	cm^3/g	0·6	0·6	0·8	1·3	2·5	2·9	2·6	7·0
CO *beyond 500°C*	cm^3/g	8	10	12	14	29	29	31	44
CO_2‖	cm^3/g	*0*	*0·4*	1·3	2·1	4·5	4·2	8·1	*8*
C_2H_6	cm^3/g	*0·5*	*2*	5·0	6·1	3·8	6·1	2·4	*3*
C_3H_8	cm^3/g	*0*	*0·5*	1·0	1·4	1·0	2·1	0·6	*0·7*
C_4H_{10}	cm^3/g	*0*	*0*	0·2	0·7	0·1	0·6	0·1	*0*
C_2H_4	cm^3/g	*0·5*	*1·0*	1·7	1·6	1·8	1·2	1·1	*1·3*
C_3H_6	cm^3/g	*0*	*0·5*	1·0	1·2	1·0	1·4	0·8	*0·7*
C_4H_8	cm^3/g	*0*	*0*	0·4	0·7	0·4	0·8	0·4	*0·2*
Total gas‖	cm^3/g	290	326	356	336	329	273	291	305
$\frac{\text{Coke residue}}{12} \times \frac{22{\cdot}4}{2 \times \text{gas}}$ ¶	C/H	3·0	2·5	2·1	2·0	1·9	2·2	2·4	2·0
Rings per mean lamella from above, using Figure 26	*R*	**19/20**	**13/14**	**8/9**	**7**	**6/7**	**9/11**	**11/14**	**7**
*Rings per mean lamella from van Krevelen***	*R*	**18**	**12**	**8**	**7**	**6**	**3**	**8**	**6**
Mean mol. wt per lamella††		680	510	390	330	310	200	400	320
Radicals per lamella	CH_3	1·1	1·3	1·4	1·2	1·2	0·5	0·9	0·9
	C_2H_5	*0·01*	*0·05*	0·11	0·13	0·08	0·03	0·07	*0·10*
	C_3H_7	*0*	*0·01*	0·02	0·03	0·02	0·03	0·02	*0·02*
	C_4H_9	*0*	*0*	0·005	0·015	0·002	0·008	0·003	*0*
	C_2H_3	*0·01*	*0·02*	0·04	0·03	0·04	0·02	0·03	*0·03*
	C_3H_5	*0*	*0·01*	0·02	0·03	0·02	0·07	0·02	*0·01*
	C_4H_7	*0*	*0*	0·01	0·02	0·01	0·01	0·01	*0*
	‡‡ OH	0	0·4	0·8	1·0	1·3	0·8	1·5	2·5
	§§ COOH	*0*	*0·01*	0·03	0·04	0·09	0·09	0·22	*0·2*
	‖‖ C=O, >—O—<	0·02	0·02	0·02	0·03	0·05	0·04	0·07	0·16
	¶¶ *Heterog. oxygen*	0·32	0·25	0·27	0·29	0·60	0·39	0·83	1·0
C (*side groups*)/C (*lamella*)		0·02	0·04	0·07	0·08	0·07	0·08	0·04	0·05

Values in italics are estimated.
* The residue has been corrected for remaining hydrogen and oxygen content, and for carbon removed as carbon monoxide above 500°C.
† Value taken from total methane/% carbon curve (*Figure 11*).
‡ Value taken from total hydrogen/% carbon curve (*Figure 12*).
§ Taken from paper by A. HAARMANN[7].
‖ Excludes carbon monoxide above 500°C, and half the carbon dioxide.
¶ Number of moles of carbon per mole of gas radicals.
** Values for *Be* and *Bm* only approximate, calculated from data given by Dormans *e tal.*[11].
†† From own values, except *Be*, taken from Dormans *et al.*[11].
‡‡ From water, see note §.
§§ From carbon dioxide.
‖‖ From carbon monoxide up to 500°C.
¶¶ From carbon monoxide above 500°C.

It is found that there is only one methyl group per lamella and that higher hydrocarbon radicals are quite rare, only about one in five lamellae having one, containing between two and three carbon atoms. In view of this it is suggested that the term 'side chain' be no longer used, as no 'chain' can have fewer than three links. The term 'side groups' is recommended.

It is assumed that the higher hydrocarbons observed do not change further on leaving the lamellae. According to H. PIETSCH[8], within the range 350° to

550°C, when the hydrocarbons are observed, ethane is stable, propane and butane are subject to degradation to the next lower hydrocarbon plus methane, and the equilibria of these reactions are well over towards the higher hydrocarbon, so that further cracking is seen to be unimportant.

Very little can be said about crosslinking, as of the groups interpreted as being present only the ether oxygen can do so. Groups such as methylene radicals, which could provide crosslinks in our scheme, appear in the methane and cannot be observed separately. This is another controversial assumption.

Owing to the statistical nature of the evidence provided, the authors have resisted the temptation to incorporate the results into a coal model, as so little is known about crosslinking.

The ring number estimation is subject to the following errors. Small amounts of tar cracking increase the amount of gas observed, leading to smaller values of R. Neglect of crosslinking leads to larger values of R, and the possibility of incomplete condensation leads to larger values of R.

D. W. VAN KREVELEN[9] calls for the determination of the number of methyl groups per carbon atom as the next step required in solving the problem of coal structure. This can be done from the present results and is given in *Table 2*, in the form of the ratio of carbon atoms in the side groups to carbon in the lamella.

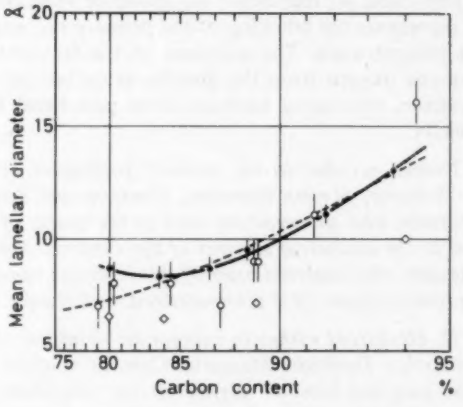


Figure 27. Mean lamellar diameter in Ångström units versus carbon content. Full line and full circles due to present authors; dotted line with no experimental points due to D. W. VAN KREVELEN *and* J. SCHUYER[6]*; open circles, to* P. B. HIRSCH[10]*; diamonds, to* R. DIAMOND[11]

The satisfactory agreement between the lamellar sizes obtained by D. W. VAN KREVELEN and J. SCHUYER's[6] method of statistical constitution analysis according to the latest revision of both authors, and the x-ray method of P. B. HIRSCH[10], is disturbed by results obtained by R. DIAMOND[11], working in Hirsch's laboratory (see *Figure 27*). Diamond obtains a distribution of lamellar sizes leading to mean values significantly smaller than those of Hirsch.

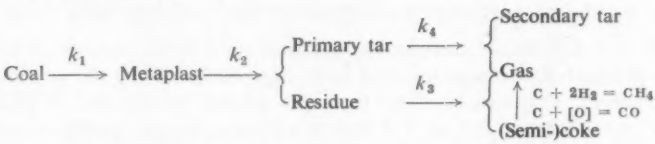
The agreement in order of magnitude between the ring numbers obtained in the present work and those from the other work mentioned is a support for the essential correctness of the assumption given above on the place of tar

in coal structure, namely, that the tar obtained under conditions of vacuum distillation is that part of the coal which is but weakly or not at all bonded to the remainder. Similar views on the origin of primary tar have been derived from X-ray and infra-red spectroscopic measurements (S. ERGUN, private communication)*.

GENERAL COAL PYROLYSIS SCHEME

The problem of coal pyrolysis and its chemical background was reviewed and thoroughly discussed by I. G. C. DRYDEN and his co-workers[13, 14]. The present authors also advanced earlier pyrolysis schemes[15, 16] which covered the reactions up to the end of plasticity. The ideas developed in this paper enable the earlier schemes to be somewhat changed and extended to cover coke formation. In what follows van Krevelen's term 'metaplast', is used rather than Fitzgerald's 'fluid coal' as the more expressive and specific term.

The new scheme is as follows:



where k_1 and k_2 are the velocity constants of the reactions proposed in the papers cited, k_3 represents the group of reactions studied in this paper, and k_4 represents the cracking of the primary tar, supposed largely suppressed in the present work. The reactions on the far right are the emission of heterogeneous oxygen from the lamella as carbon monoxide, and the autohydrogenation, producing methane from peripheral hydrogen and carbon of the lamella.

Thanks are due to the authors' colleagues at the Centraal Laboratorium, Dr Schuyer, Messrs Dormans, Huntjens and Zwietering, and particularly Mr Chermin, who advanced the work in the course of many stimulating discussions and to the analytical services of the Centraal Laboratorium, in particular, Mr Niessen, who analysed most of the 1200 gas samples. Dr Dent's permission to reproduce Figure 24 is acknowledged, with thanks.

D. Fitzgerald wishes to express his thanks to the Chairman and members of the Arthur Duckham Memorial Committee of the Institution of Gas Engineers, who awarded him the eighth Arthur Duckham Research Fellowship which supported him in the course of this work at the Central Laboratory of the Dutch State Mines for a period of over a year. He is also grateful to the National Coal Board who gave him leave of absence and every encouragement to undertake this work.

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(*Received January 1958*)

* NOTE ADDED IN PROOF. Further strong support for this view is provided by J. K. BROWN *et al.* in *J. Inst. Fuel* 31 (1958) 259, sections 3.3 and 4.1.

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Irradiation of Oxidation Products of a Bituminous Coal

C. R. KINNEY and H. L. LOVELL

Humic acid-like oxidation products have been prepared from a bituminous coal. Their loss of colour on standing in dilute sodium hydroxide solution exposed to diffused light, and the change from water insolubility to water solubility, have been examined and a possible explanation suggested. Loss-of-colour tests with oxygen excluded only are described, and the transformation was accelerated using irradiation.

HUMIC acid-like oxidation products are obtained when bituminous coals are oxidized[1] in air at 200°C. These acids slowly lose their colour on standing in a dilute sodium hydroxide solution exposed to the diffused light of the laboratory, and change from water-insoluble to water-soluble products[2]. Loss of colour proceeds more rapidly in the presence of light and oxygen. A quinone type of structure has been proposed for oxidized-coal humic acids[3], and assuming such a structure, a possible explanation for the loss of colour and the change to water solubility is inter- or intra-molcular oxidation–reduction reactions, in which the quinoid structure is reduced to the corresponding (aromatic) phenolic structure or possibly further and some other portion of the same molecule or another molecule is oxidized to balance the process.

Although the colour of the humic acids is destroyed in the presence of oxygen, oxygen is not essential for the colour to be completely eliminated, and since the results are of greater significance in its absence, as far as changes in molecular structure are concerned, only those results with oxygen excluded will be described. On the other hand, irradiation accelerates the transformation and has been used in obtaining these results. The change was followed by taking advantage of the fact that the log per cent transmittancy of a dilute sodium hydroxide solution of the humic acids gives a direct measure of their concentration, and the fact that the transmittancy of the products of the change was practically 100 per cent at 400 mμ (or higher). The products of irradiation were isolated and examined to determine molecular changes that occur during the process.

EXPERIMENTAL

Source of the humic acids—The humic acids were prepared from a Pittsburgh seam, high-volatile A bituminous coal mined in western Pennsylvania. An analysis of the coal is given in *Table 1*. The coal was oxidized in a current of air at 200°C for 234 hours and the humic acids recovered in a manner described previously[1]. An analysis of the humic acids also appears in *Table 1*.

Method used to determine concentration of humic acids in dilute sodium hydroxide solution—Plots of log per cent transmittancy versus concentration

of the humic acids dissolved in 0·1N sodium hydroxide were constructed for wavelengths ranging from 220 to 1 000 mμ and concentrations up to 200 mg/l. These plots showed a straight-line relationship between log per cent transmittancy and concentration for a given wavelength. *Figure 1* shows this relationship at 230, 300, and 400 mμ by way of example. This relationship

Table 1. Analysis of coal and humic acids

Component	*Coal*		*Humic acids*	
	As rec'd	*M.a.f.*	*As rec'd*	*M.a.f.*
Moisture	1·4		0·7	
Ash	8·6		4·2	
Volatile matter	36·9	41·0	—	
Carbon	74·4	82·6	62·5	65·7
Hydrogen	5·1	5·6	2·2	2·3
Nitrogen	1·4	1·5	1·3	1·4
Sulphur	1·8	2·0	1·0	1·1
Oxygen (by diff.)	7·3	8·3	28·3	29·5

proves that the sodium humates follow Beer's dilution law and that light absorption can be used to estimate the amount of humic acids remaining in a dilute alkaline solution.

The transformation of the humic acids when allowed to stand in dilute sodium hydroxide and when exposed to light is shown in the following

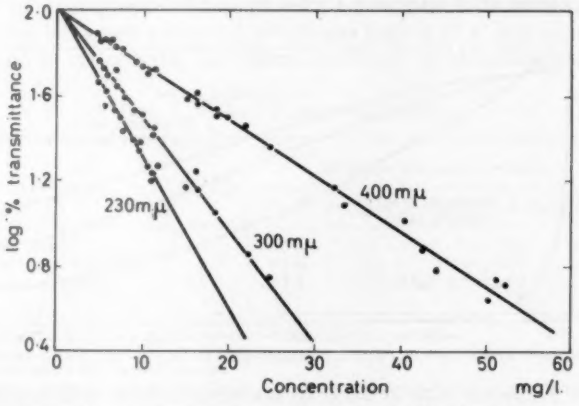

Figure 1. Log % transmittancy in the range of 230 to 400 mμ versus concentration of humic acids dissolved in 0·1N sodium hydroxide

experiments. A solution, prepared by dissolving 4·6 mg/l. of oxygen-free, 0·1N sodium hydroxide, was divided into two halves. One half was allowed to stand in a stoppered volumetric flask in a dark cabinet for 289 hours (12 days), while the second half was exposed to a focused beam of light from the tungsten filament in a microscope lamp for the same length of time. A

comparison of the absorbancies of the resulting solutions with that of the original humic acid solution is shown in *Figure 2* from 220 to 400 mμ.

Irradiation using plastic cells and a mercury vapour lamp—In the experiments described above, highly refractive, brown-coloured platelets appeared in solution exposed to light. Ignition showed that these contained but little

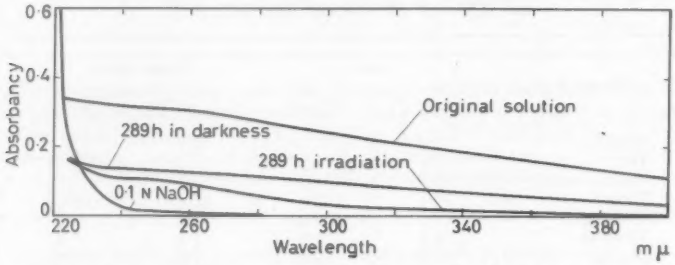

Figure 2. Effect of oxygen-free 0·1N sodium hydroxide and irradiation on absorbancy of humic acids (concentration: 4·6 mg/l.)

carbonaceous matter. Since the humic acids contained 4·2 per cent of siliceous ash, it seemed possible that this was the source of the platelets. However, a spectrographic analysis showed that the material was a borosilicate, and hence was introduced by solution of glass from the containers which were made of borosilicate glass. On substituting plastic cells for glass, no platelets formed, the mineral matter of the humic acids remaining dispersed even when all of the humic acids had been altered by radiant energy.

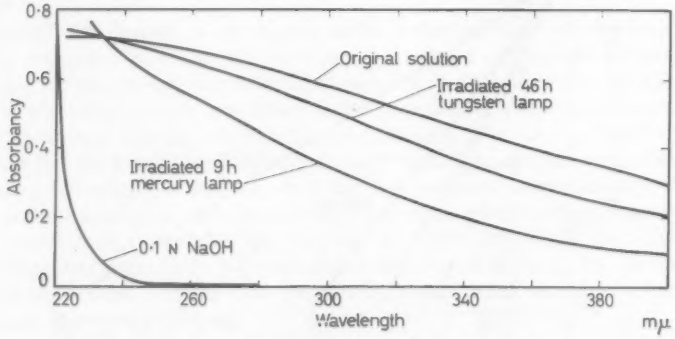

Figure 3. Effect of radiation source on absorbancy of humic acids dissolved in 0·1N sodium hydroxide (concentration: 11·3 mg/l.)

To increase the rate of change of the humic acids, focused radiation from a mercury vapour lamp[4] was used in the remaining experiments together with plastic cells. Under these conditions, 69 per cent of the humic acids, as measured by the change in absorbancy at 400 mμ, were transformed in only 9 hours in a concentration of 11·3 mg/l. of oxygen-free, 0·1N sodium hydroxide, see *Figure 3*.

Humic acid solutions of increasing concentration were also irradiated with the mercury vapour lamp, and the effect of decreasing the concentration of the sodium hydroxide investigated. The results are plotted in *Figure 4*.

Examination of irradiation products—For the purpose of examining the products of irradiation, solutions containing 11·6 mg of humic acids dissolved

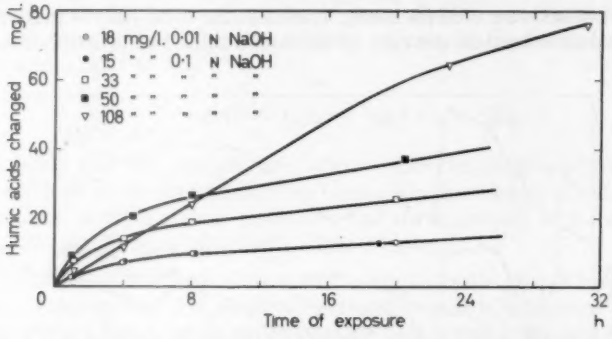

Figure 4. Effect of concentration on the quantity of humic acids changed by exposure to the mercury vapour lamp, using oxygen-free sodium hydroxide

in 0·1N oxygen-free sodium hydroxide were irradiated in Lucite cells until the brown colour was destroyed and no humic acids precipitated on acidification. Carbon dioxide was evolved, however. The acidified solutions were combined and extracted thrice with small amounts of *n*-amyl alcohol. Vacuum distillation of the alcohol left a pale yellow oil, which was kept at 65°C in a vacuum oven for 24 hours to remove the last traces of solvent. A micro-analysis of this

Table 2. Analysis of irradiation products

Product	*% Ash*	*Moisture and ash-free basis*		
		% C	*% H*	*% O, N, S (by diff.)*
Humic acids	4·2	65·6	2·3	32·1
*n-Amyl alc. extract**	9·7	61·6	7·6†	30·8
Acetone extract‡	15·7	57·8	8·1†	34·1

* Analysis made on 1 mg sample. Sample sublimed during combustion.

† Uncorrected for possible water of hydration of the siliceous mineral matter present. Maximum correction less than 0·2 per cent.

‡ Analysis made on 2 mg sample. Sample exploded during combustion with the formation of a sublimate.

fraction appears in *Table 2*, and an i.r. spectrum, made by evaporating an acetone solution of the product on a rock salt window, in *Figure 5*.

The aqueous raffinate above was evaporated to dryness, and the ground residue extracted with acetone in a Soxhlet. Evaporation of the acetone left a yellow resinous product, which contained some anisotropic crystals. A micro-analysis of this material is also given in *Table 2*, and an i.r. spectrum,

made in the same way as the alcohol extract, in *Figure 5*. A spectrum of the original humic acids is included in *Figure 5* for comparison and was made using the potassium bromide pellet technique.

The total weight of these extracts was not determined before analysis and i.r. study because the containers were too large to be weighed on the microbalance. However, over 2 mg of the alcohol extract and over 3 mg of the acetone extract were used for study. Therefore the total yield of these products amounted to at least 50 per cent of the humic acids and probably more.

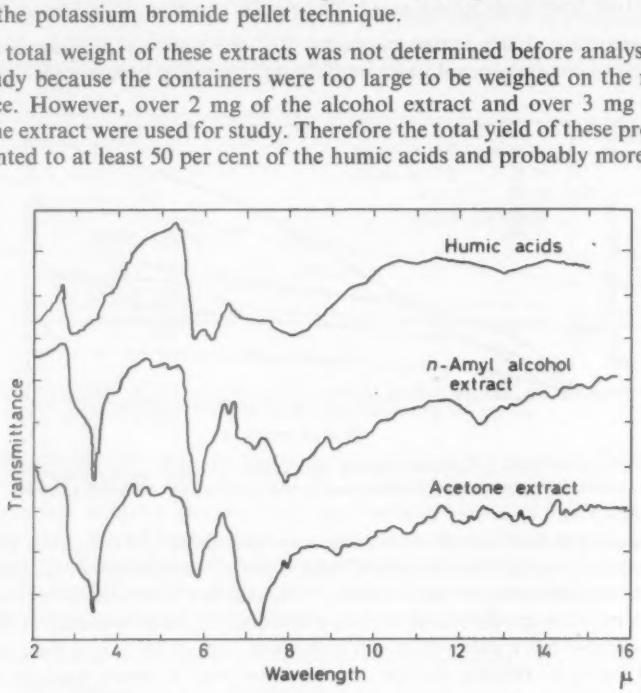

Figure 5. Infra-red spectra of humic acids, n-amyl alcohol extract, and acetone extract of irradiation products

DISCUSSION

The absorbancy of the oxidized coal humic acids dissolved in dilute sodium hydroxide falls markedly on standing in the dark at room temperatures, see *Figure 2*. The change is greatest at wavelengths of 400 mμ or higher. When the solution is irradiated for an equal length of time (289 hours) with a tungsten lamp, absorbancy falls nearly to zero at these wavelengths, demonstrating that the transformation of the humic acid structure, which absorbs in this region, is practically complete. At shorter wavelengths, there is less change in absorbancy. This shows that the products of the transformation also absorb in this region, but with less intensity. For practical conversion of the humic acids, the greater effectiveness of a mercury vapour lamp over that of a tungsten filament lamp is shown in *Figure 3*.

The weight of humic acids transformed per unit time of irradiation is nearly proportional to the concentration up to 50 mg/l. of 0·1N sodium hydroxide, *Figure 4*. However, at 108 mg/l. an inhibition of the change occurs in the early stages of irradiation. The effect does not seem to be due to the relative concentration of humic acids and sodium hydroxide, because a

solution containing 18 mg of humic acids per litre of 0·01N sodium hydroxide, corresponding to 180 mg/l. of 0·1N solution, does not show this effect. On continuing the irradiation, the quantity of humic acids converted again becomes nearly proportional to the concentration of the acids.

When the colourless, irradiated solution is acified, nothing is precipitated, showing that the humic acids have been completely altered. Carbon dioxide, however, is evolved. Although no direct proof has been obtained that light energy will bring about the usual reaction of carbonaceous materials with alkali at about 300° to 350°C[5]

$$C + 2\,NaOH + H_2O = Na_2CO_3 + 2H_2$$

it seems likely that this reaction does occur under the conditions employed. This would lead to the formation of carbonate ion from a part of each humic acid molecule, or from certain molecules, and the remainder of the molecule or molecules would be reduced with a loss of colour.

Extraction of the acidified solution with *n*-amyl alcohol gives a light yellow fraction containing nearly 8 per cent hydrogen, which is in marked contrast with the original humic acids which contain only about 2 per cent, *Table 2*. A second fraction, obtained by evaporating the aqueous solution to dryness and extracting the residue with acetone, also contains about 8 per cent hydrogen, but has less carbon and more oxygen indicating a somewhat different species of molecule. The high hydrogen content of these fractions seems to confirm the hypothesis that the loss in colour of the humic acids is due to the introduction of hydrogen. Very likely the humic acids have a polynuclear quinone type of structure[3] which should undergo reduction readily.

An examination of the i.r. spectra of the irradiation products shows strong aliphatic carbon–hydrogen bonding absorptions at about 3·4 microns, *Figure 5*, again confirming the reduced nature of the products. The spectra also show the presence of carboxyl groups by absorptions at 3·2, 5·8, 7·1 and 8·0 microns, which indicates that the acid character of the products is due primarily to carboxyl groups. Both products probably contain hydroxyl groups in addition because of the absorption shoulder at 2·9 microns. This is not believed to be due to the presence of moisture because of the care taken in evaporating the samples on rock salt windows and because of the lack of general absorption in the 6 to 7 micron region. The main difference between the two spectra lies in the strong bands at 8·0 and 7·3 microns in the alcohol and acetone extracts respectively. The band at 8·0 microns could be due to a phenolic hydroxyl. No satisfactory explanation for the band at 7·3 microns is available, but it seems likely that it is a manifestation of an hydroxyl group.

The loss of absorption at 6·2 microns in the spectra of the irradiation products, *Figure 5*, is of particular interest. The 6·2 micron band is characteristic of polynuclear aromatics including coals[6], high boiling aromatic petroleum oils[7], and coal tar pitches[8].

Other work has shown that certain quinones absorb at about 6·2 microns[9, 10], and that a part of this absorption in the oxidized coal humic acids is probably

due to this structure. Since extensive reduction has occurred it seems likely that both quinone and polynuclear structures have been reduced with loss of a large part of the absorption at 6·2 microns.

The appearance of a band at 6·6 microns in the spectrum of the alcohol extract and a shoulder band at the same wavelength in the acetone extract, *Figure 5*, together with shoulder bands remaining at 6·2 microns in both spectra, strongly suggests that the reduction has left some isolated aromatic rings unreduced in these products. The appearance of fine structure in the region of 11 to 15 microns in both spectra supports this hypothesis.

CONCLUSIONS

Oxidized coal humic acids dissolved in dilute base are transformed into carbon dioxide and light yellow water-soluble acids. The process appears to involve extensive reduction of the polynuclear quinone structure which seems to be present in these humic acids.

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(*Received May 1958*)

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The Solvent Extraction of a Low Rank Vitrain

S. M. RYBICKA

The extraction of the Northumberland vitrain D III with a number of organic solvents including ketones and N-substituted formamides is described. Binary mixtures of the ketones and formamides have been found to be better solvents than either of the pure components, the best being acetophenone–monomethylformamide and methylcyclohexanone–dimethylformamide in equimolecular proportions. Successive extraction with a range of solvents both of the coal and its ethylene diamine-soluble part is also reported.

IN the study of coal structure it is of great value if a part, preferably a major part, of the material can be brought into solution. Many organic liquids of different chemical types have been tested as coal solvents, but it is only in recent years that any systematic work has been undertaken in order to select those most suitable for extraction. I. G. C. DRYDEN's investigations[1–7] have been particularly extensive and from them he has been able to select certain important chemical characteristics that govern, in part at least, the ability of a solvent to bring low rank coals into solution. He has concluded[7] that the better solvents for coals have structures containing a nitrogen or oxygen atom possessing an available unshared pair of electrons. As an example of such compounds, Dryden has found that primary aliphatic amines, and particularly ethylene diamine, are good solvents for low rank coals. It is well known that unshared electron pairs on a nitrogen or oxygen atom can partially accept a hydrogen atom attached to another molecule to form a hydrogen bond. They may also form a coordinate linkage with another atom. Dryden has discussed both these possibilities in relation to coal–solvent interaction[7].

It is known from i.r. spectroscopic measurements[8–10] that low rank coals contain hydrogen-bonded phenolic OH groups and that the number of these groupings decreases as the carbon content of the coal increases[10–12]. There is a good correlation between the solvent power of ethylene diamine for coals and their phenolic hydroxyl content. It seems, therefore, that hydrogen-bonding between solvent and coal molecules may be an important factor in coal solution. On this basis it is possible to extend the investigations of coal–solvent interaction to a number of solvents hitherto little studied, selecting those that contain hydrogen-acceptor groups of various kinds. The present work sets out to do this, in the hope that the results, apart from their practical value, may throw some further light on the factors that govern the power of solvents to dissolve coals. In addition to the work on pure solvents the present investigation includes a number of solvent mixtures which, as far as is known, have not previously been studied. As will be seen, these should provide a new and profitable field for future workers.

Although the very extensive investigations of solvent extraction have frequently included an examination of the materials extracted, little information apart from chemical analyses is available to determine how their structures relate to one another and to the coal from which they were obtained. Studies of the i.r. spectra have the advantage over other methods that extracts obtained by different solvents can be compared not only with each other, but also with the coal before extraction and the residues. In spite of this, little i.r. work has been published. Part of the programme of the present investigation was to examine the i.r. spectra of some of the materials extracted so that some conclusions might be drawn concerning their chemical structure, particularly in relation to that of the raw coal. Reference to other i.r. work will be made when this is considered to be relevant to the discussion.

This paper discusses the solvent extraction and the subsequent paper (by J. K. Brown) the i.r. spectra of the materials extracted and the residues.

EXPERIMENTAL

The coal studied was a highly vitrainous Northumberland coal (D III)*. The analysis was: C 82·1; H 5·3; N 2·0; S 0·9; O + errors 9·7 per cent (d.m.f.). Samples of the coal oxidized with nitrogen dioxide[13] (C 64·1; H 2·6; N 4·9; O 28·4 per cent) and oxidized in air at 110°C for 160 days[14] (C 74; O 19 per cent) were also examined. All the samples were ground to − 72 B.S.S. and dried at 105°C under vacuum.

Solvents

Solvents possessing one hydrogen-acceptor oxygen atom: acetone, methylethylketone, di*iso*propylketone, methyl *n*-amyl ketone; *cyclo*hexanone, methyl*cyclo*hexanone, dimethyl*cyclo*hexanone, acetophenone.

Solvents possessing hydrogen-acceptor oxygen and nitrogen atoms: formamide, monomethylformamide, dimethylformamide.

Solvents possessing hydrogen-acceptor nitrogen atoms: pyridine, ethylene diamine.

The solvents acetophenone and monomethylformamide were obtained from Hopkin and Williams Ltd. Dimethylformamide was obtained from George and Becker Ltd. All other solvents were B.D.H. laboratory reagents and were used without further purification.

Methods of extraction

(a) *Preliminary experiments*—0·5 g of coal and 10 cm³ of solvent were mixed in a glass stoppered tube and shaken by means of a mechanical shaker for two hours. The undissolved coal was filtered off through a No. 1 Whatman filter paper and the concentration of the filtrate determined.

In these preliminary experiments not only pure solvents but also solvent mixtures containing monomethylformamide or dimethylformamide as one component were investigated. As certain of these mixtures were found to be

* Petrographic analysis: vitrinite 90·5, exinite 3·5 and carbinite 6 per cent.

good solvents a further series of tests was made to study the effect of varying the proportions of the components on the extraction yield.

(b) *Soxhlet extractions*—

(i) *Methyl*cyclo*hexanone*. 20 g of coal was extracted for 120 h in a Soxhlet apparatus under nitrogen and the yield of extract measured.

(ii) *Equimolecular mixture of methyl*cyclo*hexanone dimethylformamide*. 10 g of coal was extracted with an equimolecular mixture of methyl*cyclo*hexanone and dimethylformamide in a flask at room temperature. The suspension of the coal was filtered through a Soxhlet thimble and the residue extracted with a fresh mixture of the same solvents in a Soxhlet apparatus. The liquid and vapour compositions were equal in this extraction as the mixture formed an azeotrope (see below). An atmosphere of nitrogen was maintained over the mixture during the period of extraction. After 24 h extraction the material extracted was recovered from solution and the yield determined. The procedure was repeated for a further 120 h, a fresh batch of solvent being used.

(iii) *Equimolecular mixture of pyridine and monomethylformamide*. 15 g of coal was extracted with this solvent mixture at room temperature and the yield of extract determined. The residue from this extraction was then treated with a fresh batch of solvent mixture in a Soxhlet for a further 120 h and the yield again determined.

(c) *Successive extraction of coal*—Successive extractions of coal with a range of solvents and solvent mixtures were carried out in a Soxhlet apparatus. The solvents were heated in a water bath and maintained under an atmosphere of nitrogen. The pressure was reduced for those solvents that boiled above 100°C. The solvents were used in the order acetone, methylethylketone, acetophenone and acetophenone–monomethylformamide. After extraction with the mixture acetophenone–monomethylformamide a different procedure from that used in the previous stages was adopted. The residue of the fourth stage was again treated with the above solvent mixture, but in this case by stirring in a flask at 100°C; this resulted in a small yield of extract in addition to that found in the Soxhlet extraction (8 per cent). A further treatment of the residue from this stage with three batches of ethylene diamine, however, yielded a surprisingly large amount of extract, some 25 per cent more material being removed from the residue. The total amount extracted from the coal by the procedures described was 51 per cent.

A second extensive series of successive extractions of the coal was carried out with seven solvents. These were: (*1*) benzene (1·1 per cent extracted); (*2*) ethanol (1·3 per cent); (*3*) acetone (0·55 per cent); (*4*) butanone (1·96 per cent); (*5*) methyl*cyclo*hexanone (12 per cent); (*6*) methyl*cyclo*hexanone–dimethylformamide (24·3 per cent); and (*7*) pyridine–monomethylformamide (22·4 per cent). The total yield of extraction amounted to 63·5 per cent of the coal.

The residue after each extraction was dried *in vacuo* at 100°C for four hours. The residues from extraction with the higher boiling solvents were washed with acetone before drying.

Extraction yields

Extraction yields, expressed as a percentage of the raw coal (w/w), were determined by evaporation of from 2 to 5 ml of the solutions. The solutions were heated either on a water bath or under an i.r. lamp. The weight of dried extract was determined by direct weighing. Each of the estimations of extraction yield was made in duplicate.

Recovery of extracts from solution

Solutions were concentrated by distilling off the solvent in an atmosphere of nitrogen. After concentration the solutions were evaporated to dryness on a water bath, again under nitrogen. The solid extracts were dried *in vacuo* at 100° to 120°C until of constant weight. Microanalyses of some of the extracts were made by Drs Weiler and Strauss.

RESULTS

Preliminary experiments

(a) *Pure solvents*—In order to obtain a qualitative estimate of the amount of the coal extracted by the various solvents, as described above, a visual comparison of the colours of the solutions was made. The aliphatic ketones, acetone, methylethylketone, di*iso*propylketone and methyl *n*-amyl ketone, all gave dark yellow solutions of approximately the same colour. This indicated a low extraction yield (of the order of a few per cent). The alicyclic ketones *cyclo*hexanone, methyl*cyclo*hexanone and dimethyl*cyclo*hexanone gave solutions of deeper colour than the open-chain ketones. The methyl-*cyclo*hexanone solution was the deepest in colour. Acetophenone also gave a very dark solution, comparable in colour with the methyl*cyclo*hexanone solution. Of the formamides, formamide itself gave an almost colourless solution: monomethyl- and dimethyl-formamide solutions were dark red, the former being the darker in colour.

From these preliminary experiments it appears that the alicyclic and aromatic ketones are more powerful solvents for coal than the aliphatic ketones. Monomethylformamide and dimethylformamide also appear to be good solvents.

The nitrogen dioxide-treated coal was much more soluble in both the ketonic and formamide solvents than the parent coal. The sample was completely soluble in formamide, monomethylformamide and dimethyl-formamide to give opaque solutions. The air-oxidized coal was more soluble in the formamides than in the ketones.

(b) *Solvent mixtures*—The best solvents for the coal were selected for these studies. Binary mixtures of the aromatic and alicyclic ketones both with monomethyl- and dimethyl-formamide in the proportion 1 : 1 by volume were used and the extraction yields obtained with them were compared on a quantitative basis with the corresponding yields obtained with the pure solvents. The method of extraction was as described for the preliminary experiments. The results for the mixture acetophenone–monomethylformamide are shown in *Table 1*.

Other mixtures investigated included *cyclo*hexanone, methyl*cyclo*hexanone, dimethyl*cyclo*hexanone and pyridine with mono- and di-methylformamides.

In all cases the solvent mixtures gave higher extraction yields than either of the pure solvents. The best mixtures found were methyl*cyclo*hexanone with dimethylformamide and acetophenone with monomethylformamide.

The yields were found to vary considerably with the moisture content of the coal, the ratio of coal to solvent, and the time of extraction. In all the experiments care was taken to control these factors.

Table 1. Comparison between yields of extract obtained with 1 : 1 mixture of acetophenone and monomethylformamide and those obtained with the pure solvents

Solvent	*Percentage extraction*
Acetophenone	4·2
Monomethylformamide (MMF)	4·5
Acetophenone + MMF	12·4

The next stage was to investigate, using the same method, how the yields of extract varied with the proportions of the solvents in the binary mixture. *Table 2* shows the results of this investigation for the mixture acetophenone–monomethylformamide. The proportion of coal to solvent was 1 : 20, as in the previous experiments.

Table 2. Comparison of extraction yields for various proportions of solvents in binary mixture acetophenone–monomethylformamide

Acetophenone in mixture Per cent by volume	*Percentage extraction*	*Acetophenone in mixture Per cent by volume*	*Percentage extraction*
100	4·2	50	12·4
90	6·6	30	11·2
70	11·6	0	4·5
60	18·5		

Table 2 shows that there is a sharp increase in the amount extracted at a ratio of approximately 60 parts acetophenone to 40 parts monomethylformamide. This ratio corresponds closely to a mixture of the pure solvents in molecular proportions.

As the equimolecular mixture of acetophenone and monomethylformamide was also used in the Soxhlet extraction of the coal, it was decided to investigate its behaviour on distillation. The mixture was distilled without a fractionating column and the refractive indices of seven batches of the distillate were measured. The boiling point and refractive index of some 97 per cent of this mixture was approximately constant throughout the distillation. The mixture methyl*cyclo*hexanone–dimethylformamide was also investigated and the same behaviour found. The data are shown in *Table 3*.

The constancy of the boiling point and refractive index of a major part of the first mixture suggests that it is an azeotrope and that the composition of this azeotrope is nearly equimolecular. It is surprising that the second mixture should distil with such a narrow temperature range. The ketone used was a mixture of isomers, and perhaps homologues, and the ketone–amide

Table 3. Refractive indices and boiling points of equimolecular mixtures acetophenone–monomethylformamide and methylcyclohexanone–dimethylformamide compared with those of the pure solvents

Solvent	*Refractive index* n_{20}^{D}	*Boiling point* °C
Acetophenone	1·534	202 *to* 204
Acetophenone–monomethylformamide	1·500	182 *to* 184·5
Monomethylformamide	1·433	185 *to* 187
Methylcyclohexanone	1·452	160 *to* 170
Methylcyclohexanone–dimethylformamide	1·441	154 *to* 156
Dimethylformamide	1·431	153

mixture had a boiling point above that of the amide. Hence we cannot suggest azeotrope formation in this case. More elaborate apparatus, with a fractionating column and a sensitive method of temperature measurement is required if the nature of the binary mixture is to be established. The measurements quoted should therefore only be regarded as preliminary.

The analysis of the material extracted from the coal with acetophenone–monomethylformamide is shown in *Table 4*.

Table 4. Elementary composition (per cent) of acetophenone–monomethylformamide-soluble material obtained at room temperature

Substance	C	H	N	S	O + *errors*
Original coal	82·1	5·3	2·0	0·2	9·7
Extract	76·5	5·9	3·0	2·6	12·0

The extract is enriched in hydrogen, oxygen, nitrogen and sulphur. Although considerable care was taken to remove adsorbed solvent the odour of acetophenone could be detected in the dried sample, showing that removal was not complete. This may account for the higher oxygen and nitrogen values (from the monomethylformamide) and possibly also for the higher hydrogen content. However, the increase in the sulphur content does indicate a definite fractionation of the coal.

Soxhlet extraction of coal with solvents and solvent mixtures

Soxhlet extraction is a convenient and fairly efficient means of treating coals

with solvents at moderate temperatures and for long periods of time. The yields of extract that have resulted from this method are given for various solvents and solvent mixtures in *Table 5.*

Table 5. Yields of extract obtained with various solvents and solvent mixtures using Soxhlet extraction

Solvent or solvent mixture	*Yield of extract per cent*
Methylcyclohexanone	8·5
Methylcyclohexanone–dimethylformamide	43
Pyridine–monomethylformamide	35

The value of solvent mixtures in the extraction of the coal is once again apparent. The extraction was carried out at the boiling points of the solvents; although these were different (e.g. methyl*cyclo*hexanone 165°C; equimolecular mixture of methyl*cyclo*hexanone and dimethylformamide 154°C) the difference is in a sense that makes any temperature effects on the yield less favourable to the solvent mixture.

The elementary analysis of the methyl*cyclo*hexanone–dimethylformamide-soluble material obtained by Soxhlet extraction is shown in *Table 6.*

Table 6. Elementary compositions (per cent) of methylcyclohexanone–dimethylformamide extract obtained by Soxhlet extraction

Substance	C	H	N	S	O + *errors*
Original coal	82·1	5·3	2·0	0·9	9·7
Extract	81·1	5·3	2·2	—	11·4*
Residue	80·5	5·4	2·2	1·1	10·8

* O + S + errors.

The analyses of both extract and residue indicate a higher oxygen and lower carbon content than that of the coal; this suggests that a little solvent may have been retained. *Table 6* shows that apart from this the elementary composition of the extract is close to that of the coal.

Successive extraction of coal with series of solvents

A sample of the coal was treated successively with acetone, methylethylketone, acetophenone, and an equimolecular mixture of acetophenone and monomethylformamide. The Soxhlet extraction procedure was used, as described earlier. The yields of extract at each stage and the elementary compositions are given in *Table 7.*

The materials obtained by the successive extraction of the coal, especially with the ketones, gave solutions which on standing precipitated a film on the walls of the containers. This phenomenon has been observed by other investigators. The film could only be removed by a solvent more powerful than that

Table 7. Yields and elementary compositions (per cent) of extracts obtained by successive extraction of coal

Stage of extraction	Solvent	Method	Yield % w/w	Elementary composition						Atomic H/C
				C	H	N	S	O	Cl	
1	*Acetone*	*Soxhlet*	4·7	82·7	7·2	0·6	0·7	8·7	0·1	1·04
2	*MeEtKetone*	*Soxhlet*	2·2	78·8	6·8	1·8	1·1	10·3	1·2	0·99
3	*Acetophenone*	*Soxhlet*	9·8	81·0	5·6	1·8	1·4	10·2	0·0	0·83
4	*Acetophenone–monomethyl-formamide*	*Soxhlet*	8·4	77·3	5·0	1·5	0·0	16·2	0·0	0·78
5	*Acetophenone–monomethyl-formamide*	*Flask*	1·1	—	—	—	—	—	—	—
6	*Ethylene diamine*	*Flask*	25·0	70·9	5·5	4·5*	0·8	15·2	3·1*	[0·80‡]
	Coal D III	—		82·1	5·3	2·0	0·9	9·7	—	0·78
	Coal residue		48·0	77·6	5·3	6·1†	0·7	10·4	—	[0·66‡]

* High nitrogen and chlorine analyses probably owing to adsorbed ethylene diamine hydrochloride resulting from precipitation of extract with hydrochloric acid.
† The high nitrogen analysis of the residue suggests that some diamine was irreversibly adsorbed.
‡ Corrected to normal nitrogen content.

used in the extraction. Thus the precipitate formed from an acetone solution could only be dissolved by methylethylketone, and so on.

Successive extraction of a precipitated ethylene diamine extract

An ethylene diamine extract of the coal was successively extracted with a range of solvents in the order (*a*) benzene (*b*) ethanol and (*c*) acetone. The yields and elementary compositions of the benzene- and ethanol-soluble materials are shown in *Table 8*.

Table 8. Yields and elementary compositions of the benzene- and ethanol-soluble material obtained by successive extraction of an ethylene diamine extract

Extract	Extraction, % of ethylene diamine extract	Elementary composition					
		C	H	N	S	Cl	O + *errors*
*Ethylene diamine**	—	78·4	6·0	3·4	1·7	0·8	9·7
Benzene	16	84·3	7·4	1·4	2·1	0·0	4·3
Ethanol	14	67·4	5·9	4·3	0·9	4·1	17·4

* Approximately 12·5 per cent of the coal.

The high nitrogen content of the ethylene diamine extract probably arises from adsorbed solvent. It also appears that the high nitrogen and chlorine values of the ethanol-soluble material are a result of the removal of ethylene diamine hydrochloride which was formed during the precipitation of the ethylene diamine extract by hydrochloric acid. The most striking result is that benzene removes very much more material from the ethylene diamine extract than from the raw coal. The analyses show that the benzene-soluble material is richer in hydrogen and poorer in oxygen than either the coal or the ethylene diamine extract. This difference does not arise from adsorbed benzene as the i.r. spectrum of the material (see subsequent paper by J. K. Brown) is free of adsorption bands characteristic of that solvent.

The comparatively high oxygen content of the ethanol-soluble material is undoubtedly partly associated with ethanol retained by the extract (see succeeding paper). Nevertheless the i.r. spectra of the benzene- and ethanol-soluble materials differ in regions where ethanol does not adsorb and this suggests that some fractionation has been achieved.

CONCLUSIONS

It is clear that a wide range of solvent properties for coals is shown not only by solvents in a given class (e.g. ketones) but also by mixtures of solvents. A qualitative explanation of the variation in solvent power for a series such as formamide, monomethylformamide and dimethylformamide is possible in terms of a balance between hydrogen-bond solvent–solvent and coal–solvent interactions, but no such explanation can account for the difference between the behaviour of acetone and acetophenone or the equimolar mixture methyl*cyclo*hexanone–dimethylformamide and the pure components.

The difficulty in formulating a consistent hypothesis based on hydrogen bonding which embraces all the observations is in agreement with previous conclusions that other factors must also be operative. It strongly suggests that in certain cases such factors can be decisive. The relevance of physical effects in coal extraction is brought out by the successive extraction experiments where a large yield of ethylene diamine-soluble material was obtained after previous treatment of the coal with a range of ketones. It is likely that the relatively small, hydrogen-rich molecules removed in the early stages of successive extraction restricted access of the solvent to the larger molecules in the structure. The removal of these smaller molecules could then increase the accessibility of the internal surface of the coal to the more powerful solvent.

The advantage of binary mixtures of solvents over the pure components is shown by the considerably greater yields of extract obtained with them. The behaviour of the equimolecular acetophenone–monomethylformamide mixture on distillation has suggested that an azeotrope has been formed and this implies that the components interact, possibly resulting in a breakdown of the hydrogen-bonded polymer present in liquid monomethylformamide. It is felt that further study of binary mixtures using other powerful coal solvents could lead to a useful extension of both the theory and practice of solvent extraction work.

This work formed part of a programme of the Chemistry Department of the British Coal Utilisation Research Association on the constitution of coals, and is published by permission of the Association. The author wishes to thank Dr I. G. C. Dryden for his advice and for helpful discussions throughout the course of the work. She is also grateful to Miss J. Downs and Mr I. Officer for most valuable assistance in the experimental work.

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(*Received June 1958*)

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Infra-red Spectra of Solvent Extracts of Coals

J. K. BROWN

The i.r. spectra of a number of extracts obtained with organic solvents from a weakly caking vitrain (82 per cent carbon content), as well as the residues after extraction, have been examined in the range 700 to 4 000 cm^{-1}. They show the principal characteristics of the coal spectrum and suggest that a major part of the vitrain consists of structures of basically similar chemical type. The spectra of materials obtained with comparatively poor solvents differ most from the coal spectrum. These contain hydrogen-rich structures that have both aliphatic (alicyclic) and aromatic components. The similarities between the spectra of extracts and the parent coals in the range of carbon content 78 to 89 per cent are illustrated for two other vitrains and the implications they have in the study of solvent extracts in relation to coal structure are discussed.

S. M. RYBICKA (previous paper) has reported the results of an extensive programme of solvent extraction of a coal*. In this paper the i.r. spectra of some of the extracts and residues obtained in this work will be analysed and compared with the coal spectrum. In a later note some reference will be made to the spectra of solvent extracts of other coals, in order to permit some generalization of the conclusions.

EXPERIMENTAL

The extracts were solids and have been examined as pastes in a mulling agent. The other well known method of sample preparation, in which the solids are made into pressed discs with potassium bromide, was not used owing to the difficulty of avoiding uptake of moisture from the air during sampling. Nujol was used as a mulling agent for the region 700 to 2 000 cm^{-1} and hexachlorobutadiene for the region 2 000 to 4 000 cm^{-1}. The samples were all dried, and ground to smooth pastes in an agate mortar; long periods of grinding were necessary for the residues and the coal in order to effect the size reduction necessary for the i.r. work. The pastes were spread between rock salt plates separated by a fixed spacer. A Hilger D209 double-beam i.r. spectrometer was used to record the spectra with a 30° rock salt prism for the region 700 to 2 000 cm^{-1} and a 30° fluorite prism for the region 2 000 to 4 000 cm^{-1}. The spectra of the extracts and some of the residues are shown in *Figures 1* to *4*. The atomic H/C ratios and the percentage yields of the extracts are given in *Table 1*.

RESULTS AND DISCUSSION

The spectra will first be discussed as a whole to point out the features common to the raw coal, the solvent extracts and the residues. They will then be

* d.m.f. analysis: C 82·1, H 5·3, N 2·0, S 0·9, O + errors 9·7 per cent: petrographic analysis: vitrinite 90·5, exinite 3·5, and carbinite 6 per cent.

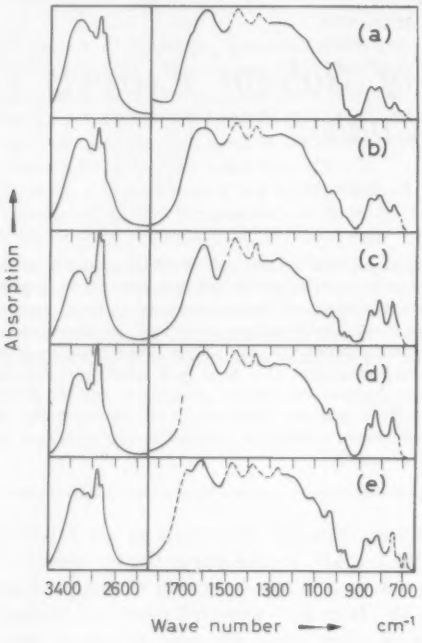

Figure 1. Infra-red spectra of extracts of Ellington High Main vitrain D3 with various solvents. (a) *Coal.* (b) *Ethylene diamine extract.* (c) *Benzene extract.* (d) *Acetone extract.* (e) *Acetophenone – N-methylformamide extract.* — — — — *Absorption obscured by Nujol and solvent*

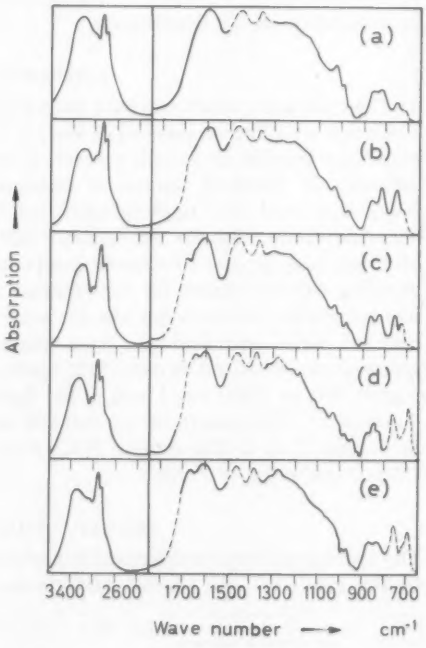

Figure 2. Infra-red spectra of successive extracts of Ellington High Main vitrain D3 using a series of ketones and ketone–formamide mixtures. (a) *D3 coal.* (b) *Extract of* (a) *with acetone.* (c) *Extract of residue from* (b) *with butanone.* (d) *Extract of residue from* (c) *with acetophenone.* (e) *Extract of residue from* (c) *with acetophenone – N-methylformamide.* — — — — *Absorption bands obscured by Nujol and solvent*

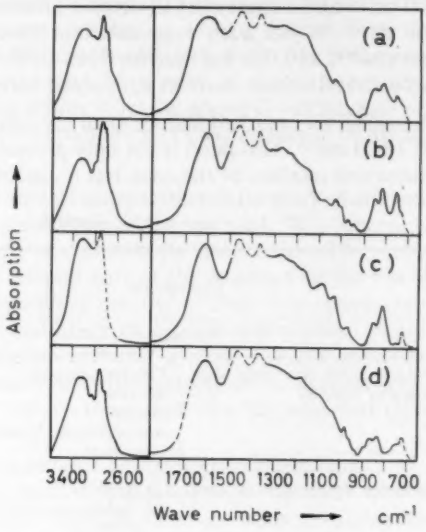

Figure 3. Infra-red spectra of successive extracts obtained from an ethylene diamine extract of D3 coal by various solvents. (a) *Ethylene diamine extract.* (b) *Benzene extract of* (a). (c) *Ethyl alcohol extract of residue from* (b). (d) *Acetone extract of residue from* (c). — — — — *Absorption obscured by Nujol and solvent*

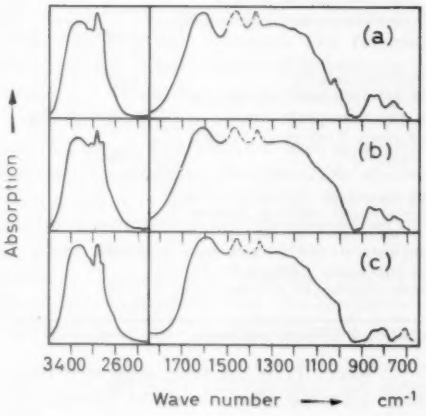

Figure 4. Infra-red spectra of residues after successive extraction. (a) *Residue of coal extracted by acetone and ethylene diamine.* (b) *Residue of coal extracted by a range of ketones.* (c) *Residue of coal after extraction by seven solvents; 60 per cent extracted.* — — — — *Absorption bands obscured by Nujol and solvent*

considered in separate sets in order to analyse the results of different extraction procedures. The latter may be classified into two main categories, namely, extraction of the raw coal by various solvents, and successive extractions of the coal and of ethylene diamine-soluble material. Finally, several residues remaining after successive extraction experiments will be discussed.

General features of spectra

The spectra of the raw coal, the solvent extracts and the residues all show a striking similarity. Each spectrum has a broad absorption band near

3 300 cm^{-1} and a somewhat ill-defined absorption region between 1 160 and 1 300 cm^{-1}. It has been suggested that these features arise from phenolic structures[1-3], and this has recently been confirmed by the acetylation of both raw coals and solvent extracts with acetic anhydride (see, for example, ref. 4).

A second very marked feature in all the spectra is a strong absorption band near 1 600 cm^{-1}. This band is not only present in the spectra of all the solvent extracts and residues of the coal, but is also charateristic of bright coals over

Table 1

Description		*Atomic H/C ratio*	*% Yield*
Coal		0·78	
Extracts from raw coal with various solvents	*Ethylene diamine*	(0·80)	12·3
	Acetone	1·04	4·7
	Benzene	1·05	
	Acetophenone–N-methylformamide	0·93	12
Successive extracts from coal	(a) *Acetone*	1·04	4·7
	(b) *Butanone extract of residue from* (a)	0·99	2·2
	(c) *Acetophenone extract of residue from* (b)	0·83	9·8
	(d) *Acetophenone–N-methylformamide extract of residue from* (c)	0·78	9·5
Successive extracts from ethylene diamine-soluble material	(e) *Benzene-soluble*	1·05	16
	(f) *Ethyl alcohol extract of residue from* (e)	1·05	14
	(g) *Acetone extract of residue from* (f)	0·96	3·5
Residues after extraction	*After successive extraction with acetone and ethylene diamine*		
	After successive extraction with five solvents (50% extracted)	(0·66)	
	After successive extraction with seven solvents (60% extracted)	0·78	

Atomic H/C ratios corrected to normal nitrogen content shown in parentheses.

a wide range of carbon content[3, 5-8]. Recently, it has been suggested that this absorption band arises either from aromatic ring vibrations brought up in intensity by the presence of ether linkages, or from carbonyl groups chelated to hydroxyl groups possibly in hydroxy–quinonoid structures[3]. The possibility that absorption in the 1 600 cm^{-1} region was associated in part at least with polycyclic quinones or anthrones was put forward in earlier i.r. studies of coal extracts by D. HADŽI[9]. Both types of structure present in the same molecule or different molecules could, of course, contribute to the intensity of the 1 600 cm^{-1} band. The reductive acetylation of extracts of coals has been shown to effect a marked reduction in the intensity of the 1 600 cm^{-1} band; this observation is consistent with the assignment of a considerable part of the intensity to chelated carbonyl groups[4, 10]. It is therefore reasonable to conclude that such groupings are present in all the materials studied.

The similarities already discussed in the spectra are associated with oxygen groupings. The remaining features present in all the spectra arise from aromatic C—H bonds (700 to 900 cm^{-1}) and CH_2 and CH_3 groups (near 3 000 cm^{-1}). The latter groupings may be present in aliphatic or alicyclic structures. The absorption bands arising from the above C—H linkages show marked differences in intensity between different extracts and will be discussed later.

It should be noted that the spectra of some extracts have marked absorption in addition to that present in the spectrum of the raw coal. This occurs in the region 1 650 to 1 700 cm^{-1} and is undoubtedly associated with carbonyl groups. The groupings may be a small part of the structure of the raw coal and remain undetected in its spectrum because of their low concentration. However, the fact that the marked absorption is limited to those materials extracted by solvents which contain carbonyl groups makes it much more likely that the effect is associated either with a chemical reaction between the solvent and the extract or with small amounts of strongly adsorbed solvent.

Materials extracted from coal by solvents of different chemical types

Figure 1 shows the spectra of material extracted from the coal with four solvents of different chemical types. The spectra of the benzene- and acetone-soluble materials differ most from the spectrum of the raw coal. This is not unexpected as benzene and acetone are much less powerful solvents than either ethylene diamine or the acetophenone–*N*-methylformamide mixture and probably extract materials less representative of the whole coal. The chief difference is the considerably stronger aliphatic (or alicyclic) C—H and aromatic C—H absorption in the benzene and acetone extract spectra. The increase in the proportions of these groups is in accord with the higher H/C ratios (*Table 1*). The weakest hydrogen-bonded OH absorption band (near 3 000 cm^{-1}) occurs in the spectrum of the benzene-soluble material; the oxygen content is also lowest for this extract. From what has already been said above concerning the interpretation of certain features of the spectra, this means that the benzene extract contains the lowest amount of phenolic material. The ethylene diamine extract has a spectrum most closely approaching that of the coal, the similarity in the pattern of aromatic C—H absorption between 700 and 900 cm^{-1} being particularly striking.

Products of successive extraction of the same sample of coal with a range of ketones

The spectra of these extracts are shown in *Figure 2*. In the successive extraction experiments solvents of increasing power were used, acetone being the weakest and the mixture acetophenone–*N*-methylformamide the strongest of the series. Each of the solvents removed material with aromatic, aliphatic (or alicyclic) and oxygen-containing components. As already noted, the spectra of these materials are very similar to the spectrum of the raw coal. The extracts differed mainly in the proportions of aromatic C—H and aliphatic (or alicyclic) C—H bonds. The materials obtained by successive extraction of the coal contained progressively less aromatic and aliphatic (or alicyclic) hydrogen, as shown by a reduction in intensity of the absorption pattern at

3 000 cm^{-1} and between 700 and 900 cm^{-1}. There is a corresponding decrease in the atomic H/C ratios from the material soluble in acetone to that soluble in the acetophenone–*N*-methylformamide mixture.

Products of successive extraction of ethylene diamine-soluble material

Successive extraction experiments of the type carried out on a sample of the raw coal have also been applied to the ethylene diamine-soluble material. Here the three solvents, benzene, ethyl alcohol and acetone, were used. The spectra of the materials removed by these solvents are shown in *Figure 3*. The spectrum of the material extracted by benzene from the ethylene diamine extract is closely similar to that of material extracted by benzene from the raw coal (*Figure 1*). There is also a close correspondence between the spectrum of that part of the ethylene diamine extract soluble in acetone when used as first solvent (not shown) and the material extracted directly from the coal by acetone. This suggests that the benzene- and acetone-soluble portions of the coal and of the ethylene diamine extract have similar structures.

The spectrum of the portion of the ethylene diamine extract soluble in ethyl alcohol has a very strong OH absorption band near 3 300 cm^{-1} [*Figure 3*(c)]. This may be the result of a preferential extraction of phenolic material or, more probably, it is due to the presence of adsorbed alcohol in the extract. It should be noted that the chemical analysis shows a high percentage of oxygen (previous paper).

The acetone-soluble material obtained from the residue after extraction with benzene and ethyl alcohol has a spectrum [*Figure 3*(d)] that differs markedly from that of the product of extraction of raw coal with acetone [*Figure 1*(d)]. The aromatic C—H absorption pattern in the region 700 to 900 cm^{-1} and the aliphatic (or alicyclic) C—H bands near 3 000 cm^{-1} are much weaker in the spectrum of the acetone-soluble part of the diamine residue. These absorption bands are also much weaker than in the first stage of the successive extraction [i.e. with benzene, *Figure 3*(a)]. This observation agrees with the successive extraction experiments on the raw coal. Material rich in aromatic and aliphatic hydrogen is removed in the early stages of extraction; further extraction of the residues with other solvents yields material with progressively less. This change is accompanied by the expected decrease in the H/C ratios [*Table 1*, (e) and (g)].

Residues after successive extraction

Figure 4 shows the spectra of three residues remaining after successive extraction of the coal with solvents. There are minor differences between the spectra; the main features closely resemble those of raw coal. The spectra of the residue from the successive ketone extractions and the more extensive extractions with seven solvents have a somewhat more diffuse absorption in the region 1 000 to 1 100 cm^{-1} and the pattern of aromatic C—H absorption is weaker than in the residue from acetone and ethylene diamine extraction. The intensity of the absorption bands associated with oxygen groupings differs very little although the residues represent fractions varying from approximately 90 to 40 per cent of the coal.

General remarks

Apart from the changes in intensity of certain absorption bands discussed above, the spectra of all the materials examined are strikingly similar. The spectra of the successive extracts and residues show that the groupings associated with i.r. absorption occur throughout the coal, thus establishing the close relation between the chemical structure of solvent extracts and of the parent coal.

The conclusions drawn from this work on extracts of one coal may be summarized as follows:

(*1*) The absorption bands observed in the i.r. spectrum of the coal are present in the spectra of all the extracts

(*2*) The absorption pattern of the raw coal is representative of a major part of its structure

(*3*) The spectra of materials removed from the coal by poor solvents differ most from the coal spectrum. The extracts contain structures rich in aromatic and aliphatic (or alicyclic) hydrogen

(*4*) Materials richer in hydrogen than the average are removed from the coal and also from its ethylene diamine-soluble part by successive extraction

(*5*) Powerful solvents extract material from the coal which is only partly soluble in poorer solvents. This soluble part has a spectrum very similar to that of the substances obtained directly from the coal with these weaker solvents.

It is evident that clear-cut fractionation of the coal into substances of widely differing chemical types has not been brought about by any of the solvents or series of solvents studied. The i.r. spectra of aromatic hydrocarbons are markedly different from those of aliphatic or alicyclic hydrocarbons and these, in their turn, are readily distinguished from the spectra of phenolic structures. No such distinction can be made for the solvent extracts. It is a striking fact that the chemical groupings that give rise to i.r. absorption in the coal spectrum are present in all the extracts and residues. Extraction may remove some material that is radically different in chemical structure from the bulk of the coal but, with the solvents and vitrains discussed in this work, 'coal-like' material always appeared to predominate.

SOLVENTS EXTRACTS OF OTHER COALS

In the work described above an account has been given of a detailed examination of an extensive series of extracts of one coal. In the course of chemical work in this laboratory many extracts of a number of highly vitrainous British coals (of carbon content in the range 78 to 90 per cent) have been prepared from time to time, and the spectra of these materials were determined at the time of preparation. The same relation between the spectra of extracts and those of the parent coals has always been observed: that is, a marked similarity in overall pattern with certain differences in detail, as described above for the Northumberland coal. Two examples out of the many available

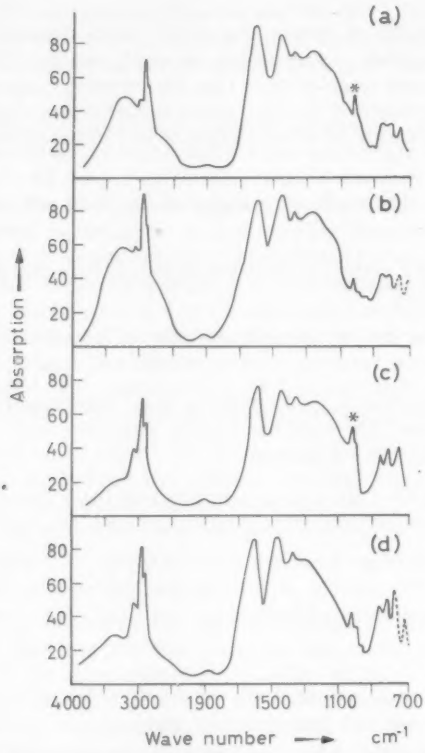

Figure 5. Infra-red spectra of D9 and D13 coals and their pyridine extracts. (a) *D9 coal.* (b) *Pyridine extract of D9 coal.* (c) *D13 coal.* (d) *Pyridine extract of D13 coal.* — — — — *Absorption partially associated with solvent.* * *Absorption partially associated with ash*

are presented in *Figure 5* to illustrate this statement; the spectra of pyridine extracts of two coking coals are there compared with the spectra of the whole coals. No comment on the spectra, beyond what is said about those of the extracts of the Northumberland coal, is called for. The analyses of the extracts and the parent coals are given in *Table 2.*

Other workers have found correspondences between the spectra of a Sardinian[11] and an Assam[12] coal and their extracts but some of the spectral detail appears to have been obscured owing to solvent interactions.

Table 2. Analyses of coking coals and their pyridine extracts

Material	*Extract w/w % of coal*	*Per cent by weight*				
		C	H	N	S	O + *errors*
D9 coal	—	86·0	5·3	2·2	0·7	5·8
Pyridine extract of D9 coal	12·1	83·7	6·0	2·7	—	7·6*
D13 coal	—	88·9	5·1	1·5	0·7	3·9
Pyridine extract of D13 coal	2·7	85·9	5·7	2·0	—	6·4*

* O + S + errors.

IMPLICATIONS FOR CHEMICAL STUDIES OF COAL STRUCTURE

The close relationship between the i.r. spectra of solvent extracts and those of the parent coals establishes a correspondingly close relationship between their functional groupings. The similarity in the structure of their carbon skeletons is also suggested but cannot be established unequivocally—any more than it can with the parent coals—owing to the overall complexity of the spectra. As expected the relationship is closest for extracts obtained with powerful solvents but also persists to a marked extent in the products from extraction with the weaker solvents. There is no implication that the similarities in spectra will persist as the proportion of the coal extracted is further reduced nor that the conclusions can be applied to coals other than vitrains in the range of carbon content 78 to 89 per cent. But with these limitations it does follow that *qualitative* information, e.g. about the existence of functional groups or important features of structure, can be extrapolated from extract to whole coal without serious risk of error. It would clearly be unwise to take *quantitative* measurements made on extracts, for example, the concentration of functional groups, or of molecular weight, to apply to the whole coal unless additional evidence can be adduced that this is justified.

It is obviously preferable to study the chemical structure of coal by taking the whole coal rather than an extracted part. However, it may sometimes be more convenient to work with solvent extracts in solution: indeed for some experiments this is the only possible course. The above discussion makes clear the limits within which the study of extracts is informative.

This work formed part of a programme of the Chemistry Department of the British Coal Utilisation Research Association on the constitution of coals, and is published by permission of the Association. The author wishes to thank Dr I. G. C. Dryden for his guidance and encouragement at all stages of the work. The infra-red spectra were obtained in the Department of Colloid Science, Cambridge, by kind permission of Dr N. Sheppard and Professor F. J. W. Roughton, F.R.S.

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Randalls Road, Leatherhead, Surrey (*Received June 1958*)

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Interpretation of the Intensities of X-Rays Scattered by Coals

S. ERGUN and V. H. TIENSUU

X-Ray studies of the structure of coals are reviewed, and various interpretations of the X-ray intensity bands of coals are discussed. The study covers all ranges of scattering angle and emphasis is placed on quantitative interpretation. Original data were obtained to aid in the interpretations and suggestions are made concerning promising lines of attack in future investigations.

X-RAYS have been employed as a physical tool in structural studies of coals. Most of the earlier workers, notably C. MAHADEVAN[1–3], H. G. TURNER and H. V. ANDERSON[4], P. CORRIEZ[5], T. SCHOON[6,7], I. D. SEDLETSKII[8], W. SCHEER[9], and H. E. BLAYDEN, J. GIBSON and H. L. RILEY[10] focused their attention on scattering at medium and large angles. Scattering patterns obtained by these workers revealed two (or more) diffuse peaks at the positions of the most prominent graphite bands and the peaks became less diffuse as the carbon content of the coal increased. These observations led most of them to suggest that small graphitic ring clusters exist in coals, and that coals become more graphite-like as coalification proceeds. Although supported by later work, these deductions were regarded by crystallographers as tentative explanations rather than established facts.

In addition to coals, Blayden *et al.*[10] studied carbonization products of various coals and their banded constituents and of some pure organic compounds. They postulated that coals contain aromatic layers about 20 to 30 Å in diameter, aligned parallel to their near neighbours at distances of about 3·5 Å, thus forming stacks some 14 to 17 Å in height. Qualitatively, these postulates have been supported by later workers; quantitatively, the results were found to be seriously in error. A special feature of this work was the interpretation of the (002) band which arises from the stacking of planar aromatic ring clusters. An adjacent band at a spacing of 4 to 5 Å has been observed by Mahadevan[2]. Blayden *et al.* observed the latter band with a sample of Northumberland coal and called it the γ band. The intensity curves these workers plotted contained asymmetric (002) peaks. They contended that the asymmetry was due to the γ band even when a peak at its position was absent. Therefore, they resolved the peak into a symmetrical (002) band and a γ band. The method of plotting of these workers was entirely arbitrary and no valid conclusions can be drawn for the asymmetry of the (002) peaks in their curves. Subsequent work showed the γ band to be caused principally by the exinite component (spores, resins, etc.) of coal.

Following Blayden *et al.*, V. I. KASATOCHKIN and co-workers[11–15], U. KITAZAKI[16,17] R. PAMPUCH[18], and others have studied X-ray scattering intensities of coals to follow changes in the structure with metamorphism

and/or carbonization. In general, their deductions confirmed those of earlier workers. Studies of Kasatochkin included carbon black, activated carbon and humic acid, in addition to coals of various ranks and of different petrographic origin. He observed that the intensity pattern of spore-matter (a petrographic component, generally called exinite, of durain and clarain type coals) contained the γ band[11]. He also found that a humic acid, obtained from oxidation of coal, when subjected to 5000 atm pressure, gave rise to the γ band. He attributed the γ band to packing of aliphatic side chains, i.e. liquid-like packing induced by pressure.

Interest in x-ray scattering from coals at small angles developed somewhat later. The first study of this type was made by H. Brusset, J. Devaux and A. Guinier[19] and by H. Brusset[20]. They observed scattering at small angles, continuously increasing with decreasing angle. The scatter was interpreted as arising from micelles, believed to consist of molecules of humic substances composed of aromatic ring clusters surrounded by a carbonaceous material of different electron density. The micelles, presumably spherical or nearly spherical, were stated to have diameters between 40 and 200 Å. The views of these investigators were not shared by later workers, who examined scattering at both low and high angles.

Studies of D. P. Riley[21] confirmed scattering of x-rays by coals at small angles. In addition, Riley observed that some coals exhibited a broad but well defined band having a peak position corresponding to a spacing of about 25 to 28 Å. This observation led Riley to state that these coals consisted of closely packed spherical particles having a mean diameter of 30 to 35 Å, and he referred to them as 'liquid-type' scatterers. Riley believed that coals that did not give rise to this peak did not possess a regular type of structure and he termed them 'gas-type' scatterers.

The first of two papers by J. B. Nelson[22] dealt with x-ray scattering from coals in the angular range corresponding to spacings between 2·5 and 250 Å. He called the band at 3·4 to 3·8 Å (the 002 band of earlier workers) 'the outer maximum'. Nelson found that the peak position of this band progressively changed with carbon content of the vitrinite and that the *d* spacing, extrapolated linearly to 100 per cent carbon content, coincided with the interlayer spacing of graphite. He also confirmed an observation made by earlier workers that the band showed a progressive sharpening with increase in rank (carbon content) of coal; nevertheless, he contended that this band did not constitute unique evidence for the existence of condensed aromatic nuclei in coals. However, this band constitutes strong supporting evidence once the existence of condensed aromatic rings in coals is established by x-rays or otherwise.

Nelson found no evidence for the existence of a γ band in the vitrinites he examined. However, as was observed by Kasatochkin[11] earlier, an exinite-rich component of a coal (about 90 per cent exinite) that Nelson examined gave rise to the γ band; therefore, he stated that exinite inclusions could produce γ band effects. These findings have been confirmed by other workers. Nelson confirmed the existence of a well defined band, which he termed 'inner-scattering maximum' at about 20 Å spacing (cf. Riley[21]). This band

became noticeable first for vitrinites having a carbon content of about 83 per cent and became most prominent for a vitrinite having 90·5 per cent carbon. He stated that the band corresponded to a statistically preferred distance of not less than 20 Å but did not offer an exact interpretation for the band. By extending his measurements to smaller angles, Nelson showed that Riley's division of coals into two distinct groups, 'liquid-type' and 'gas-type' scatterers, was a consequence of the failure to extend the observation to smaller angles. Nelson attributed the continuous scattering at very small angles to differing electron densities of the continuous phase in the coal and to the network of submicroscopic pores. His qualitative analysis of the data by the methods of H. BRUSSET, J. DEVAUX and A. GUINIER[19], C. G. SHULL and L. C. ROESS[23], and H. L. RITTER and L. C. ERICH[24], did not yield satisfactory results.

In all the previous work, x-ray scattering intensities at angles corresponding to spacings less than 4 Å were explained on the basis of condensed aromatic ring clusters. This might be termed 'indexing' the pattern, and similar indexing was applied earlier to carbon blacks. However, B. E. WARREN[25] had shown that such indexing is more or less intuitive and that the necessary structural information can be obtained, without making any *a priori* assumptions as to the crystallinity of the material, by calculating the atomic distribution function. In a quantitative study of carbon black, Warren used the Fourier integral analysis developed by B. E. WARREN and N. S. GINGRICH[26] from earlier work of F. ZERNIKE and J. A. PRINS[27] and confirmed the existence of interatomic distances close to those within a single graphite layer. R. E. FRANKLIN[28] applied the same technique in a study of a non-graphitic carbon (polyvinylidene char) and confirmed the presence of small graphite-like layers in the char. To obtain information about the spatial distribution of the layers, i.e. size, spacing, and inter-particle distance, she obtained the particle distribution function by excluding the (*hk*) reflections in the integral analysis. It remained for J. B. NELSON[29] to examine the structure of vitrinites by obtaining the atomic distribution function. Nelson's experiments covered six vitirinites having carbon contents ranging from 77 to 89 per cent. He stated that the Fourier transforms of these vitrinites would be consistent with aromatic nuclei having not more than four fused rings, i.e. less than 7 Å in size. Compared with estimates by earlier workers who had used x-rays [10] and other physicochemical and statistical methods[30–33], nuclei containing less than four rings appeared to be rather small. Recent theoretical developments, however, supported Nelson's view.

In an x-ray study of carbonization of coals, V. I. KASATOCHKIN and L. L. RAZUMOVA[34] calculated atomic distribution functions of two cokes and stated that the coke obtained at 1 100°C had a lower amount of carbon in the side chains than the coke prepared at 500°C. In interpreting the molecular structure of coals and cokes, these authors regarded non-graphitic carbon atoms as belonging to side chains, hence having a regular arrangement. They were at variance with Franklin[28] who, in estimating the fraction of carbon in graphite-like layers, assumed the remainder of the carbon to be roentgenamorphous.

Advances in quantitative interpretations of x-ray scattering intensities of coals in medium- and high-angle regions are due to B. E. WARREN[35], J.

BISCOE and B. E. WARREN[36], R. E. FRANKLIN[28], P. B. HIRSCH[37], and R. DIAMOND[38–40]. Warren developed the theory of diffraction in random layer lattices and derived equations giving both the form and absolute intensity of the (*hk*) bands in terms of the layer dimension and the position of the peak. Biscoe and Warren used this theory in analysing the (10) reflections of a carbon black and observed good agreement. In a detailed study of a non-graphitic carbon (polyvinylidene char), Franklin analysed the (11) and (10) reflections and compared the results with those obtained from atomic and particle distribution functions. She observed that, excepting inter-particle spacing, the Warren equations yielded more precise information and required less labour.

Application of these developments to coals is due to Hirsch. Using the Warren equations, he estimated bond lengths, layer sizes, and percentage of carbon in the form of layers for a series of vitrinites. His calculations yielded layer diameters ranging from 7 Å for a coal containing 78·3 per cent carbon to 9 Å for coal with 89 per cent carbon. With further increase in carbon content, the layer size increased rapidly. For the proportion of carbon in ordered form, i.e. in layers, he reported values ranging from 65 to 80 per cent. For the medium angle region, Hirsch developed a novel Fourier inversion technique which showed that the layers occur partly as single layers and partly in groups of two, three, or more stacked parallel to each other. Moreover, he demonstrated that there was a preferred orientation of the layers parallel to the bedding plane of the coal bed. It is interesting to note that, in a later study, L. L. RAZUMOVA, V. I. KASATOCHKIN and M. P. VOLAROVICH[41] observed a re-orientation in the structure of a coal sample after it had been subjected for a short period to a unidirectional pressure of about 20 000 atm. The graphite-like layers were preferentially oriented with their normals in the direction of the active pressure.

In his studies, Hirsch was also concerned with the 20 Å band and scattering at smaller angles. Regarding the 20 Å band, his work confirmed Nelson's findings. He further observed that the band became diffuse again for the anthracites. He stated that the 20 Å band was due to ordering on a scale of 20 Å and that the degree of ordering parallel to the bedding plane was slightly greater than that normal to the bedding plane. As to the nature of the order, he considered the band to be a consequence of 'liquid-type' packing of the layer groups; i.e. the statistically preferred distance between groups of two to three layers (8 Å in size) was about 20 Å.

Hirsch employed a double-crystal spectrometer technique to investigate scattering at very small angles. From the shape of the curves, the presence of close packed micelles or dilute systems of spherical micelles or pores less than 5 000 Å in diameter was ruled out. He also observed that total scattering was larger for specimens cut normal to the bedding plane than for those cut parallel to it and stated that this would be expected from a system of disc-like cracks oriented preferentially parallel to the bedding plane.

The spherical integration in the treatment of B. E. WARREN[35], and in later treatments of random layer structures by A. J. C. WILSON[42] and G. W. BRINDLEY and J. MERING[43], involved some approximations. Although these

approximations introduced little error with large layers, R. DIAMOND[38, 39] noted that their effect could be serious if the layers are very small; therefore, he computed theoretical data for the intensity of x-rays diffracted from randomly oriented small layers of various sizes by using the Debye radial distribution function. He developed a matrix method[40], based on the principle of least squares, to analyse the observed intensities in terms of linear combinations of theoretical data belonging to different size groups.

The method of Diamond was designed to obtain a maximum amount of information from the (11) band. Its sensitivity to modifications in the assumptions was checked. Possible effects of hydrogen and oxygen atoms, elongated molecules, and holes in the molecules were considered. Diamond showed that five-membered rings and aliphatic bridges effectively terminated a layer. He also showed that innermost atoms of edge groups are included in the layer in calculating layer sizes and that they contribute to amorphous scattering to the extent of about 50 per cent of their weight. The latter finding showed that it is necessary to allow for the presence of edge atoms in deducing the number of rings in the aromatic ring clusters from the layer diameters obtained using the Warren equations or Diamond's matrix method. Therefore, Hirsch's estimates of the number of rings must be modified to some extent. For example, for high volatile coals[44], the number of rings may lie between 1 and 3 instead of 4 and 6. Another interesting feature of the method of Diamond is that it permits determination of average bond length in the aromatic nuclei with great accuracy.

It has been thought that studying carbonized coals, coal extracts, vacuum pyrolysis products, and coals hydrogenated at low temperatures might throw some light on the structure of coals. X-Ray studies of carbonized coals[10, 34, 38] were directed mainly toward exploring the mechanism of carbonization. The observed changes in the x-ray diagrams with carbonization undoubtedly helped the development of the present methods of interpretation of x-ray scattering intensities of coals[38]. L. CARTZ *et al.*[45] made an x-ray examination of ethylenediamine extracts and residues of vitrains and observed changes at low angles for all extracts and slight changes in the residues of only low rank coals. At high angles, x-ray diagrams of both the extracts and residues were found to be very similar to those of untreated samples. Low angle scattering by extracts was explained by 'crystallization' of the extracted material to form a 'micro-pore' structure as occurs in coking coals. S. ERGUN[44] studied vacuum distillation products of a vitrinite (84 per cent carbon) by x-rays and observed that the results of intensity profile analyses of the products did not support the existence of side chains in appreciable quantities in the vitrinite and that the results could be tentatively explained if the vitrinite is conceived as a polymer of small (1 to 3 rings), partially oriented planar units. Changes in the x-ray diagrams upon hydrogenation proved to be very revealing. S. ERGUN and I. WENDER[46] studied coals reduced with lithium in ethylenediamine and observed that the (002) band was shifted to lower angles (from 3·6 Å to 4·8 Å) and that important changes had occurred at high angles. The average bond length deduced from the (11) reflections had increased from 1·395 Å to 1·47 Å. The changes in the x-ray patterns were explained by the displacement of the carbon atoms of the aromatic nuclei

as a result of hydrogenation, the shifting of the (002) peak being the result of the increased distance between parallel but buckled layers. They further observed that the γ band encountered with the exinite component of coals could arise from parallel alicyclic layers. From the above investigations, it appears that systematic studies of hydrogenated coals or coal extracts could lead to better understanding of the structure of coals.

Several developments in the theories of scattering at small angles[47–52] may find application in the interpretation of pore structure and surface area of coals. Most of these developments are treated in recent texts by A. GUINIER and G. FOURNET[53], A. GUINIER[54], and by G. FOURNET[55]. V. LUZZATI[56,57] and J. L. SOULÉ[58] have recently presented theories of multiple scattering. In his work on the scattering of X-rays by dense systems, G. POROD[50,51] had shown that the asymptotic behaviour of the low angle scattering curve depends essentially on the specific boundary surface between the two media of which the scattering material is composed. V. LUZZATI[57] and J. L. SOULÉ[58] have shown that the laws of Porod are valid also for multiple scattering. The theoretical findings of these workers should also greatly facilitate the experimental technique and permit better interpretation of inhomogeneities.

From the foregoing survey it is seen that the interpretations of the intensities of X-rays scattered by coals involved the (*hk*) reflections of graphite-like layers, the (00*l*) reflections of the layers, small angle scattering, and the inversion of the observed intensities to obtain atomic and/or particle distribution. To elucidate these interpretations, the intensity bands will be considered in more detail.

(a) *The (11) band*

Diamond[38] and Hirsch[37] showed that this band arises mainly from hexagonal ring structure and is diffuse because the hexagonal layers are small. P. SCHERRER[59] was the first to suggest that the size of a crystallite (simple cubic) could be calculated from the width of the bands at half intensity. He derived the relationship

$$\beta = C\lambda/L \cos\theta \quad \ldots\ldots [1]$$

where β is a measure of band width, λ is the wavelength of the X-radiation, L is the crystallite diameter, θ is the Bragg angle, and C is a constant. Later workers, notably M. VON LAUE[60], derived similar formulae for other crystals and Warren[35] for random layer lattices.

Theoretical considerations[35,38] showed that each peak extends indefinitely on the high angle side so that the intensity never falls to background between peaks; therefore, definition of widths of these bands becomes ambiguous. Diamond[38] observed that if a width is measured along a line parallel to two consecutive minima on a graph of absolute intensity (Compton scattering deducted) versus $s\ [= (2/\lambda) \sin\theta]$ at a height midway between the peak and the line joining these minima, an empirical correlation $\beta L = 1{\cdot}422$, for $L > 8$ Å, can be observed between the width thus measured and the layer size L for the (11) band. This correlation is analogous to using $C = 0{\cdot}7$ in equation 1.

As the widths of these bands are ill defined quantities, information obtained from the widths is questionable. Therefore, Hirsch made a profile analysis of the (11) band by comparing experimental curves quantitatively with curves calculated from the Warren equations[35] for single, randomly oriented graphitic layers of various diameters [Franklin[28] describes the application of the Warren equations to the (11) band].

Aromatic ring clusters present in coals are small; therefore, the applicability of the Warren equations was questioned by Diamond[38]. For small aromatic molecules, direct calculation of the (*hk*) reflections becomes feasible by the use of the Debye radial distribution function[61]:

$$\frac{I(s)}{f^2(s)} = J(s) = \sum_r \frac{n(r)}{N} \frac{\sin 2\pi rs}{2\pi rs} \quad \ldots\ldots [2]$$

where $I(s)$ is the intensity of coherent scattering in electron units, $f(s)$ is the atomic scattering factor, $J(s)$ is the intensity in atomic units, $n(r)$ is the number of interatomic distances (vectors) of length r within the layer, irrespective of direction, N is the total number of atoms in the layer, and s is defined by

$$s = (2/\lambda) \sin \theta \quad \ldots\ldots [3]$$

Diamond calculated[39] the values of $J(s)$ for a series of aromatic molecules having from 11 to 288 carbon atoms, i.e. ranging in size from 5·8 to 30 Å.

The x-ray scattering, I_e in electron units, from a ring cluster of a given size group i can be expressed as

$$I_e(s) = f^2(s)J_i(s) + C(s) \quad \ldots\ldots [4]$$

where $f^2(s)J_i(s)$ represents the coherent scattering and $C(s)$ the Compton scattering. Equation 4 applies to amorphous carbon as well, when $J(s) = 1$ at all values of s. Scattering from a mixture of size groups and from amorphous carbon can be expressed as a linear combination of individual contributions, i.e.

$$I_e = f^2 \sum_i x_i J_i + C \quad \ldots\ldots [5]$$

In equation 5, the explicit reference to s has been dropped and x_i denotes the fraction of atoms in size group i. If it is assumed that coal contains amorphous carbon atoms and aromatic ring clusters of various sizes, then it becomes possible to determine the distribution of carbon in terms of amorphous atoms and those in ring clusters of the sizes chosen. Designating the ratio of intensity in arbitrary units to that in electron units by k, the observed intensity I_a, in arbitrary units, can be expressed as

$$I_a = f^2 \sum_i \alpha_i J_i + kC + v \quad \ldots\ldots [6]$$

where $\alpha_i = kx_i$, $\Sigma\alpha_i = k$. and v is the residual error. Substitution of

$$B_i = f^2 J_i + C$$

in equation 6 yields

$$I_a = \sum_i \alpha_i B_i + v \qquad \ldots . [7$$

Equation 7 permits calculation of the coefficients α_i provided a sufficient number of intensities (corresponding to different values of s) is obtained. Using a large number of I_a values, the principle of least squares can be applied advantageously. This approach forms the mathematical basis of the method of Diamond. For standardizing treatment of data, Diamond specified the range of s values, viz., $s = 0{\cdot}66$ to $0{\cdot}96$, as well as layer sizes. The resulting solution is in matrix form and yields the values of the α_i's directly.

In calculating the $J(s)$ values of aromatic molecules (cf. equation 2), Diamond used a value of 1·4174 Å for the bond length r. The mean bond lengths of coals generally do not coincide with this value; therefore, the observed intensity curves and the curves obtained using the calculated size distributions show a horizontal displacement. Diamond showed that the displacement is related to the deviation of the true bond length from the assumed, thus permitting calculation of the mean bond lengths in coals.

The above approach to intensity analysis is well suited for a system made up of aromatic ring clusters and completely amorphous carbon. The internal structure of the aromatic ring clusters should be perfectly regular. These assumptions are to be regarded as only partially true. As stated above, Diamond confined the profile analysis, i.e. fittings, to the angular range $s = 0{\cdot}66$ to $0{\cdot}96$. Outside the fitted range, the calculated and observed curves differ somewhat. The discrepancy in the region of the (10) band points to irregularities in the layers or that the layers are part of a larger imperfect unit. The absence of appreciable quantities of aliphatic side chains in coals suggests that these layers are linked to each other very closely, forming an irregular polymer[44]. In using the method of Diamond, it is possible to correct for oxygen, or any other element, if it is assumed that such atoms are entirely roentgenamorphous. On the other hand, oxygen atoms directly attached to aromatic carbons are expected to contribute heavily to the size of the layer. Thus a correction for the presence of oxygen atoms as roentgenamorphous would be an over-correction for the peripheral oxygens. Making no correction at all for the presence of non-carbon atoms introduces serious errors for oxygen-rich coals, as was anticipated by Diamond[38].

The matrix method is sensitive to perturbations in the intensity curves caused by x-ray fluorescence, line broadening, peak-displacement, polarization, etc. These effects should properly be eliminated or corrected for. Frequently one obtains negative coefficients for one or more size groups, for which Diamond offered several explanations and suggested alternative solutions. Fortunately, in the alternative solutions the fraction of roentgenamorphous carbon and mean layer size appear more or less invariant. However, the fraction of the roentgenamorphous carbon derived from the analysis of the (11) band is considerably less than that derived from the (002) band. This will be discussed later.

(b) *The (10) band*

This band, like the (11) band, arises from hexagonal ring structure. Biscoe and Warren[36], Blayden *et al.*[10] and L. E. ALEXANDER and E. C. SOMMERS[62] preferred to use this band in place of the (11) band. Unless there is a high degree of stacking of the layers, the (10) band is affected almost over its entire range by the (00*l*) reflections. For coals, the (00*l*) variation can be regarded as an oscillation about the mean of the (00) reflections (cf. Diamond[38]). In order to utilize the (10) band in analysing two-dimensional ordering in coals, it is necessary to correct for the effects of the (00*l*) reflections. Then this band can be used to check the results obtained from the (11) reflections.

(c) *The (002) band*

This band is the most prominent x-ray band of coal. Nelson[22] showed that its peak position changes progressively with carbon content (of vitrinite) and that, when extrapolated to 100 per cent carbon, it coincides with the peak position corresponding to the inter-layer spacing of graphite. Establishment of the presence of aromatic ring clusters in coals[29, 37] and steric considerations lead to the conclusion that this band results from groups of parallel layers, each group containing only a very few layers.

Various analytical techniques have been used to study the (002) band. Earlier workers used the rather crude method of studying peak-broadening. Franklin[28], in dealing with a carbon prepared by pyrolysis of polyvinylidene chloride at 1 000°C, treated the (002) band as a modulation of the (00) reflections (cf. Warren[35]) and expressed the intensity in atomic units due to this band as

$$I'_{002} = I'_{00}(1 - x_A)\,\Sigma P_N \frac{\sin^2(\pi N d_N s)}{N \sin^2(\pi d_N s)} \quad \ldots . [8]$$

where x_A is the fraction of carbon in amorphous form, d_N is the inter-layer spacing in groups of N parallel layers, and P_N is the fraction of the aromatic carbon contained in the group, ΣP_N being equal to 1. The value of I_{00} was obtained from the Warren equation

$$I'_{00} = 0{\cdot}0606/s^2 \quad \ldots . [9]$$

The total observed intensity I', in atomic units, is then given by:

$$I' = \{(1/k)I_a - C\}/f^2 = x_A + I'_{002} \quad \ldots . [10]$$

Substituting equation 10 into 8 and rearranging

$$\frac{I' - x_A}{1 - x_A}\frac{s^2}{0{\cdot}0606} = \Sigma P_N \frac{\sin^2(\pi N d_N s)}{N \sin^2(\pi d_N s)} \quad \ldots . [11]$$

The left side of equation 11 can be plotted versus s and the resulting curve can be analysed in terms of N and P_N using the right side, if the inter-layer spacing d_N is more or less invariant with N. This approach constitutes Franklin's method. Equation 11 shows that the resulting curve should be symmetrical about an axis passing through the value of s corresponding to

d_N. However, when this equation was used in the analysis of the (002) bands of the vitrinite components of two coals examined in the present study, the resulting curves were not symmetrical; the low angle sides of the curves were less steep and the minima on the high angle side were higher.

I'_{00} defined by Warren and Franklin is identical with the $J(s)$ value of Diamond:

$$I'_{00} = 0{\cdot}0606/s^2 = J \qquad \ldots . [12]$$

Therefore, the product of J and s^2 should be constant and equal to 0·0606. Diamond[38] showed that this is not strictly true. Inasmuch as the (002) band can be expressed as a modulation of the (00) reflection, it would be more rigorous to substitute

$$\{1/(1 - x_A)\} \sum_{i \neq A} \delta \, x_i J_i$$

in place of $0{\cdot}0606/s^2$ in equation 11, to give

$$\frac{I' - x_A}{\sum\limits_{i \neq A} x_i J_i} = \Sigma P_N \frac{\sin^2 (\pi N d_N s)}{N \sin^2 (\pi d_N s)} \qquad \ldots . [13]$$

This modification did not overcome the asymmetry of the curves of the two vitrinites examined.

To use the foregoing equations, the amorphous carbon content x_A and the scaling factor in electron units are generally obtained from the remote (11) band or the (10) band. Alexander and Sommers[62] noted that the correct value of x_A must be used to obtain a symmetrical curve when the left side of equation 11 is plotted versus s, and utilized the equation to determine the value of x_A that yields a symmetrical curve. Amorphous carbon contents of two vitrinites and a fusinite employed in the present study were found to be 52, 65 and 40 per cent as determined by Alexander's method. When the (11) bands of the same samples were analysed (Diamond's method), the amorphous carbon contents obtained were 35, 37 and 24 per cent, respectively. Since coals are admittedly complex in structure, the discrepancy might be attributed to this complexity rather than to some specific factors involved in using either or both of the methods. Therefore, the x-ray diagram of a petroleum coke was analysed by the above methods; the (002) band again yielded a higher value of amorphous carbon content, i.e. 23 per cent compared with only 4 per cent obtained from the (11) band. The difference between the results by the two methods is large and several factors could contribute to it:

(*1*) Factors other than an incorrect value of amorphous carbon content may contribute to the asymmetry of the (002) band. For example, inhomogeneities (pores, etc.) on the 10 Å scale would contribute to the scattering on the low angle side of the (002) peak but hardly at all on the high angle side. Such an effect would simulate roentgenamorphous material;

(*2*) Error may be involved in converting scattering from arbitrary into electron units;

(*3*) Some layers may be separated by a greater distance so that the interlayer spacing cannot be regarded as constant. Increase in the spacing for the small stacks would give rise to an enhancement of the low angle side of the (002) band at the expense of the high angle side.

The analysis of the (002) band by the use of Warren–Franklin equations should lead to useful information provided the above discrepancies are resolved. Franklin and later Alexander and Sommers[62] demonstrated that the distribution of layers in groups, i.e. singlets, doublets, triplets, etc., could be estimated from a profile analysis of the band. S. S. POLLACK and L. E. ALEXANDER[63] applied the principle of least squares to obtain the most probable stacking distribution.

Hirsch[37] developed a cosine transform for estimating stacking distribution

$$P(u) = 2\int_0^\infty (I/f^2)\cos 2\pi su \, ds \qquad \ldots . [14]$$

where $P(u)$ is a one-dimensional function relating to the atomic centres and I is the experimentally determined intensity. In equation 14, u is treated as distance and s as reciprocal distance. Diamond[38] showed that I_{002}/f^2 in place of I/f^2 should be used in equation 14

$$P(u) = 2\int_0^\infty (I_{002}/f^2)\cos 2\pi su \, ds \qquad \ldots . [15]$$

Once a transform is obtained by the use of equation 15, the relative number of stacks tied in groups of two, three, etc. (not including single platelets) can be determined from the amplitudes. One of the problems involved in the use of the above method concerns the determination of I_{002}. Diamond used the relationship developed by Warren[35]

$$I(s) = KI_{00l}/s^2 \qquad \ldots . [16]$$

where

$$K = 2/3\pi\sqrt{3}l^2 = 0{\cdot}12252/l^2 \qquad \ldots . [17]$$

and l is the bond length. The transform applies only to coherent scattering; therefore, some provisions should be made to subtract amorphous and Compton scattering, the latter becoming noticeable at $s > 0{\cdot}2$. The problem posed here, although less important, is the same as in the Warren–Franklin method already discussed. Another problem concerns the cut-off, i.e. the upper limit of s for the transform. This problem, however, is always present when Fourier transforms of limited ranges are performed.

The (002) region is the most prominent part of coal patterns; it should be investigated thoroughly. The Warren–Franklin profile analysis and Hirsch–Diamond cosine transforms constitute two basic approaches to studying stacking of random-layer lattices. However, it does not appear that coals

satisfy completely the conditions of applicability of these methods in their present state of development.

(d) *The γ band*

The γ band is a broad maximum occurring in the angular range corresponding to 4 to 5 Å. It is generally observed with exinite components of coals[11, 22, 45, 64]. Ergun and Wender[46] found that reduction of vitrinites with lithium in ethylenediamine displaces the (002) band to lower angles, i.e. to spacings where the γ band of exinites occurs.

A definite interpretation of the γ band has not yet been established. Kasatochkin[11] thought the band arose from the packing of aliphatic side chains. Cartz *et al.*[45] suggested that it arises from irregular packing of the aromatic layers and that the greater spacing of this band compared with that of the (002) band may be due to buckling of the layers or to the presence of more aliphatic material around the edges of the aromatic systems. Based on the experiments on the hydrogenation of vitrinites, Ergun and Wender[46] stated that the γ band could arise from parallel alicyclic layers.

The shift of the (002) band to lower angles with hydrogenation for high rank coals offers an opportunity for an authentic interpretation of x-ray patterns of coals at low angles.

(e) *The 20 Å band*

Riley[21] stated that the 20 Å band was related to the diameter of the close-packed spherical particles composed of aromatic lamellae. Hirsch[37] attributed the band to inter-particle scattering for which 20 Å is the preferred separation. J. K. Brown and P. B. Hirsch[65] attributed the band to the form factor for independent scattering units having electron densities at the core greater than the mean value, 20 Å being the diameter of such units. An essential feature of the form factor postulate is that the scattering units must be encased in a shell of less than average density in addition to having more than average density at the core.

In the course of the present study, x-ray scattering intensities of four major petrographic components (exinite, vitrinite, micrinite and fusinite) of a high volatile bituminous coal (Hernshaw) were examined. Only the x-ray pattern of fusinite did not show a band at about 20 Å. Cartz *et al.*[45] had observed that in the exinite-rich concentration of a black durain, both the band at 20 Å and the (002) band were considerably reduced in intensity relative to the γ band. The exinite examined presently had a very suppressed (002) band, but the 20 Å band remained relatively strong. A definite interpretation of this band would be useful for elucidating the structure of coals.

(f) *Scattering at very small angles*

The diffuse scattering around the primary beam at angles corresponding to spacings greater than 25 Å, i.e. $0 \leqslant s < 0{\cdot}04$, is referred to as small angle scattering. This scattering is interpreted in terms of pores, cracks, and other inhomogeneities. Recent developments[50, 51, 56, 57] may permit a thorough examination of the inhomogeneities of coals. The experimental work in the present study was not fully extended to this region.

SUMMARY

From the foregoing review and analysis, it can be concluded that studies of x-ray scattering intensities have thrown some light upon the physical structure of coals. The presence of aromatic ring clusters was established by obtaining atomic distribution functions from Fourier integral analysis of the observed intensities (Nelson) and by direct comparison of the observed intensities with those calculated using the Warren equations (Hirsch) and also using the Debye radial distribution functions (Diamond). Profile analyses indicated that not all of the carbon atoms are part of the aromatic rings. Quantitative methods were developed (Hirsch–Diamond) for estimating bond lengths, fraction of carbon in planar rings, size distribution of rings, and stacking of planes. These methods permitted analysis of changes in structure due to metamorphism, degree of carbonization, and petrographic make-up.

In the development of quantitative methods, some assumptions were involved; viz., carbon atoms were regarded as either belonging to aromatic ring clusters or randomly distributed; the ring clusters were presumed to be perfect in their internal structure; and, except for a tendency of neighbouring planar units to align parallel, the planes were believed to be randomly distributed in space. These assumptions appear to be only partially true, for it has not been possible to fit the observed intensity curves with those calculated over a wide angular range. Estimates of roentgenamorphous carbon obtained from the (11) and (002) bands do not agree.

Most primary degradation products of coals, such as low temperature tar and coal hydrogenation oils, contain five-membered rings. Indanols are found in phenols obtained from coal tar. These findings strongly suggest that coals may contain five-membered rings in appreciable quantities. In interpreting x-ray scattering intensities of coals, the existence of five-carbon rings has not been considered in detail by crystallographers. A thorough study will require some theoretical work on the scattering from five-membered rings attached to aromatic nuclei.

Qualitative interpretations of scattering intensities at low angles are very sketchy. Other than a tendency of adjacent planar units to align parallel, not much is known about how the layers are arranged. According to the most widely accepted concept, roentgenamorphous material (Hirsch) or side chains (Kasatochkin) are attached to the layers and parallel groups of layers from electron-dense regions, i.e. micelles. However, x-ray studies of vacuum distillation products (Ergun) suggest a polymeric rather than micellar structure. Little is known about the roentgenamorphous material.

Better understanding of the structure of coals and development of more valid quantitative interpretations of x-ray scattering intensities are more or less interdependent. Systematic investigation of the structure of coal by other physical and chemical methods and improvement in the techniques and interpretation of amorphous scattering should be pursued simultaneously.

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(*Received April 1958*)

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Chemical Constitution of Coal VI—Optimum Conditions for the Preparation of Sub-humic Acids from Humic Acid by Ozonization

F. Dobinson and G. J. Lawson

Conditions have been determined which afford the largest yield of sub-humic acids when humic acid dissolved in equivalent sodium hydroxide solution is oxidized with ozone. The yield is reduced if the amount of alkali used to dissolve the humic acid is greater than the theoretical equivalent.

In a previous communication[1] it was shown that humic acid from outcrop coal could be readily oxidized with ozonized oxygen to produce good yields of water-soluble acids (sub-humic acids). A series of small-scale oxidations showed that the yield of sub-humic acids depended upon the amount of oxidizing agent consumed but it was not possible to apply the results to larger scale work other than in an empirical manner, because the uptake of ozone was calculated from the rate and time of flow on the assumption that its utilization was complete. The humic acid was dissolved in alkali before ozonization, and it was noted that the amount of alkali employed had a significant effect on the yield of sub-humic acids. A 'cyclic' ozonization apparatus was developed which allowed precise control of the amount of ozone consumed in an oxidation and permitted complete recovery of the oxidation products so that carbon balances could readily be obtained. The present paper describes the use of this apparatus first to determine optimum conditions for the production of sub-humic acids by ozonization of humic acid dissolved in an equivalent amount of alkali, and secondly to examine the effect of an excess of alkali on the course of the oxidation.

Humic acid was obtained from a Warwickshire outcrop coal, C.65, by extraction with alkali, using the method described in Part I of this series[2]. Two samples, isolated from the same coal sample but at different times, were used in the present studies. Their elementary analyses, which differed slightly, are shown in *Table 1*, together with the equivalent values (E_1), which were determined by potentiometric titration (glass electrode) with hydrochloric acid of solutions in excess of decinormal sodium hydroxide. Titration of solutions in stronger (1·4N) sodium hydroxide gave lower values (E_2); the E_1 value for a humic acid sample was found to be approximately twice the E_2 value.

The ozonization apparatus[1] consisted essentially of a pump driving oxygen, in a closed circuit, successively through an ozonizer, the reaction vessel, and a suitable absorption train for recovery of the gaseous oxidation products.

The degree of ozonization was regulated by control of the amount of oxygen consumed within the apparatus.

To determine the degree of oxidation which gave maximum yields of sub-humic acids, a series of experiments was carried out in which portions of humic acid, approximately 10 g each, were dissolved in equivalent sodium

Table 1. Analyses of humic acids

Sample	*Ash* %	*Elementary analysis (% d.a.f.)*					E_1
		C	H	N	S	O (*diff.*)	
D7	4·9	62·6	2·8	1·7	0·5	32·4	186
D355	7·0	63·8	2·9	1·6	0·5	31·2	165

hydroxide and oxidized with ozone corresponding to amounts of oxygen ranging from 6 l. to 10 l. The results of the series of oxidations are shown in *Table 2*. At the end of each oxidation the amounts were determined of unreacted humic acid, carbon monoxide (as carbon dioxide), sub-humic acids soluble in ether, and sub-humic acids insoluble in ether but soluble in acetone. The ether-soluble acids were isolated in two fractions by partial acidification of the reaction mixture followed by complete acidification.

Table 2. Oxidation of humic acid with various amounts of ozone

Ozone consumed (as litres of oxygen)	*Time of reaction*	*Humic acid taken g*	*Humic acid recovered† g*	*Yield of ether-soluble sub-humic acids, g*		*Yield of acetone-soluble sub-humic acids g*	*Yield of carbon monoxide (as CO_2, g)*
				Fraction F_1	*Fraction F_2*		
6·0	50 *h**	9·500	1·918	1·583	1·597	1·732	0·045
7·25	36 *h*	9·925	2·552	1·551	2·061	1·693	0·253
8·0	48 *h*	9·534	0·928	1·626	2·967	1·628	0·325
8·75	3 *days*	9·500	0·606	0·611	1·448	1·328	0·350
10·0	9 *days*	9·515	1·058	0·000		0·113	0·362

* The rate of this oxidation was slower than expected because a partial blockage developed within the apparatus and restricted the flow of ozonized oxygen.
† This material contained a considerable amount of sodium chloride.

Both fractions of the ether-soluble sub-humic acids were produced in maximum yield when 8 l. of oxygen was used for the oxidation. The yield of acetone-soluble acids was greatest with 6 l. of oxygen, and decreased as the consumption of oxidant increased; however, the combined yield of ether- and acetone-soluble sub-humic acids was greatest when using 8 l. of oxygen per 10 g of humic acid. The proportions of reactants are in good agreement with the approximate optimum amounts calculated from earlier work[1]. The amount of carbon monoxide produced increased with the amount of oxygen used. It does not appear to be a primary oxidation product of humic acid since the extent of its production is not proportional to the consumption of humic acid. It must arise therefore by the further oxidation of water-soluble

sub-humic acids. The reaction time increased from about 2 days for the oxidation with 6 l. of oxygen to about 3 days for that with 8·75 l.; the oxidation with 10 l. took considerably longer. This last oxidation yielded no ether-soluble acids, and only a small amount of acetone-soluble material; this result was to be expected since the theoretical volume of oxygen necessary to oxidize the humic acid completely to carbon dioxide and water was 10·3 l. It thus appears that no substantial part of the humic acid molecule is stable indefinitely to ozone in the presence of water.

To investigate the effect of alkaline conditions upon the oxidation, experiments were carried out in which the humic acid was dissolved in amounts of alkali 2, 10 and 300 per cent in excess of the theoretical equivalent calculated from value E_1. The rate of consumption of oxygen showed a marked decrease as the alkali was increased. *Table 3* shows the results of these experiments,

Table 3. Ozonization of humic acid in the presence of various amounts of sodium hydroxide

Sodium hydroxide in excess of theoretical equivalent %	*Time of reaction*	*Ozone consumed (as litres of oxygen)*	*Humic acid taken g*	*Humic acid recovered g*	*Yield of ether-soluble sub-humic acids, g*		*Yield of acetone-soluble sub-humic acids g*	*Yield of acetone-insoluble sub-humic acids*	*Yield of carbon monoxide (as CO_2, g)*
					Fraction F_1	*Fraction F_2*			
Nil	36 *h*	7·25	9·925	2·552	1·551	2·061	1·693	3·583	0·253
2	50 *h*	7·0	9·500	2·885	1·201	1·614	1·406	2·778	0·319
10	3 *days*	6·5	9·500	2·972	1·152	1·427	1·114	2·148	0·250
300	4 *days*	6·0	9·521	2·978	0·329	0·273	0·364	*Not det'd*	0·104

together with those of a similar oxidation in which no excess of alkali was employed. The yields of all the sub-humic acid fractions decreased sharply as the alkali was increased; this trend was not altered when the yields were calculated on the basis of the humic acid actually consumed in the oxidation. The sub-humic acids are not completely recovered by extraction with ether and acetone since some are insoluble in acetone. The possibility was considered of the use of an excess of alkali resulting in larger yields of acetone-insoluble acids but when their yields were calculated in three cases they also decreased with increase in alkali. The first fraction (F_1) of ether-soluble acids isolated from the ozonization using exactly equivalent alkali was a pale yellow solid, but when an excess of alkali was employed the corresponding products were brown in colour. The second fraction (F_2) of ether-soluble acids, and the acetone-soluble acids, were dark brown resinous materials. It was noticed that some of the sub-humic acids from the experiments employing an excess of alkali evolved nitric oxide on drying; this effect appeared to be due to traces of nitrogen in the oxygen used, since it was prevented by the use of electrolytic (i.e. nitrogen-free) oxygen. The traces of nitrogen were shown to give rise to nitric acid in the reaction vessel, and the sodium nitrate thus formed during ozonization of humic acid presumably liberated nitric acid on acidification which was extracted by ether together with the sub-humic acids. The nitric acid presumably then reacted with the sub-humic acids to give a labile product which later decomposed with the production of nitric oxide. The evolution of nitric oxide must, however, indicate a difference in the nature of the sub-humic acids obtained under different reaction conditions,

and hence in the course of the oxidation, because nitric acid ought similarly to be present in the acids from the oxidation using equivalent alkali. These, however, produced no detectable nitric oxide.

The effect of an excess of alkali was further investigated by means of a series of carbon-balance oxidations, in which 10 g portions of humic acid were dissolved in 1, 1·5, 2 and 3 equivalents of alkali before ozonizing with ozone equivalent to 8 l. of (nitrogen-free) oxygen. After each oxidation the distribution was determined of the carbon of the original humic acid amongst the oxidation products (carbon dioxide, carbon monoxide, volatile acids, water-soluble non-volatile acids, and recovered humic acid). The results are shown in *Table 4*. The amount of carbon appearing as recovered humic acid

Table 4. Carbon-balance ozonization of humic acid dissolved in various amounts of alkali

Percentage of carbon appearing as:	*Amount of alkali*			
	Equivalent	1·5 × *equivalent*	2 × *equivalent*	3 × *equivalent*
Recovered humic acid	3·9	25·8	26·0	27·2
Carbon dioxide	50·1	42·0	48·2	49·1
Acids volatile in steam (acetic acid)	2·7	2·2	2·1	1·6
Carbon monoxide	1·4	0·9	0·9	0·9
Water-soluble non-volatile acids	45·6	30·4	23·8	21·7
Totals	103·7	101·3	101·0	100·5
Calc. on humic acid consumed:				
carbon dioxide	52·0	56·4	64·9	67·4
acids volatile in steam (acetic acid)	2·8	2·9	2·9	2·2
carbon monoxide	1·5	1·2	1·2	1·2
water-soluble non-volatile acids	47·4	40·8	32·0	29·7
Totals	103·7	101·3	101·0	100·5

increased sharply from 3·9 to 25·8 per cent on changing the alkali from 1 to 1·5 equivalents, but altered little with further increase. The relationships between the other products of the ozonizations are best considered relative to the amount of humic acid carbon converted to water-soluble and gaseous products. It is seen (*Table 4*) that as the amount of alkali is increased the carbon appearing as carbon dioxide increases gradually at the expense of the sub-humic acids, which show a corresponding decrease. The yields of acetic acid and of carbon monoxide are relatively unaffected by changes in the concentration of alkali.

It thus appeared that a fairly small excess of alkali produced a marked change in the amounts of the reaction products. This might be due to an alkali-catalysed change in the structure of the humic acid, or to an alteration in the mechanism of the oxidation process. Since ozone is known to be decomposed by alkaline conditions there is a third alternative, namely that the changes might result from a reduction in the effective concentration of ozone. This alternative, which is in agreement with the reduced speed of reaction observed when an excess of alkali is used, would require that the

rate of oxidation of humic acid to sub-humic acids were reduced to a greater extent than that of the further oxidation of sub-humic acids. The effect of an excess of alkali in the ozonization reaction is being further studied.

It was concluded that the maximum yield of sub-humic acids, and also the best recovery of carbon in this form, could be obtained when 10 g of humic acid was dissolved in exactly equivalent alkali, using value E_1, and ozonized with ozone equivalent to 8 l. of oxygen. These conditions were therefore employed for preparative oxidations, the results of which will be described in a later communication.

Some further study was made of the relatively large amount of humic acid recovered after ozonization employing an excess of alkali. As will be seen from *Table 6* solutions employing up to twice the equivalent (E_1) amount of alkali become acidic during the course of the oxidation. This fact does not account for the recovery of relatively large amounts of unoxidized humic acid which it might be thought would be precipitated from solution and so would escape substantial oxidation because the most acidic conditions (using equivalent alkali) gave the least recovery of humic acid. A further possibility was that the sodium ions introduced with the excess alkali precipitated sodium humate by the common ion effect, and that this solid material did not react readily with the gaseous ozone. However, it was shown in separate experiments that the amount of sodium humate that could be so precipitated was very much smaller than the amount of humic acid recovered in the oxidations.

The residual humic acid from ozonization with three equivalents of alkali was analysed for carbon and hydrogen, and its acid equivalent was determined by back titration both from a solution in 0·1N alkali (E_1) and from solution in 1·4N alkali (E_2). These values were closely similar to those determined in the same way for the original humic acid (*Table 5*). When the residual humic acid

Table 5. Comparison of original and residual humic acids

Humic acid	*Analysis (% d.a.f.)*		*Equivalent values (ash-free)*		*Ash %*
	C	H	E_1	E_2	
Original	63·8	2·9	153	76·4	7·0
Residual	57·6	3·0	158	79·9	25·1

was dissolved in equivalent alkali (using value E_1) and ozonized in the usual way, it consumed ozone much more slowly than did the original humic acid under the same conditions. It thus appeared that the residual humic acid, although analytically similar to the original, was relatively more resistant to ozone. It is possible that part of the humic acid molecule is rendered ozone-resistant by the action of excess alkali, and that when the remaining, unaltered, part has been converted to sub-humic acids these sub-humic acids are themselves oxidized more rapidly than the resistant humic acid, which will

therefore be found in the reaction vessel when the required amount of ozone has been absorbed. The nature of the changes induced by alkali is still under investigation.

EXPERIMENTAL

Ozonization apparatus

The cyclic ozonization apparatus has been fully described in a previous communication[1]. The oxygen reservoir was filled from a cylinder, and traces of carbon dioxide were removed before the gas entered the ozonizer. The oxygen used in earlier experiments was prepared by fractionation of air, and contained nitrogen as an impurity; in the carbon-balance ozonizations electrolytic (nitrogen-free) oxygen was used. All ozonizations were carried out at room temperature.

Oxidation of humic acid with various amounts of ozone

Typical procedure: An exactly equivalent amount (calculated from value E_1) of sodium hydroxide solution (approximately 1N) was added to an accurately weighed portion (about 10 g) of humic acid D 7, which had previously been stored *in vacuo* over phosphorus pentoxide. Sufficient water was added to increase the total volume to about 200 ml, and the mixture was shaken mechanically for about 3 h to ensure complete solution. The solution was transferred quantitatively to the reaction vessel, and adjusted to the normal working volume (about 300 ml). The vessel was then attached to the ozonization apparatus, which included the appropriate absorption trains for carbon dioxide, and carbon monoxide, and the oxygen reservoir system was arranged to deliver the required amount of oxygen. Ozonized oxygen was pumped around the cycle at a speed of about 15 l./h, the oxidation being terminated automatically when the required amount of oxygen had been consumed as ozone. The time of reaction was noted, or estimated as accurately as possible for oxidations which terminated during night-time. In the course of the oxidation using 6 l. of oxygen the gas flow became reduced and unusual pressure differences built up in the apparatus; this was afterwards traced to a partial blockage which developed in the carbon dioxide absorption train. The time of reaction for this oxidation was thus longer than was expected, and was not strictly comparable with those for other oxidations.

After each oxidation the absorption tube which removed carbon dioxide originating as carbon monoxide was weighed, and the contents of the reaction vessel were transferred to a larger flask. Standard hydrochloric acid was added in sufficient quantity to neutralize 55 per cent of the sodium hydroxide used initially to dissolve the humic acid, and the mixture was evaporated to dryness *in vacuo* and the residue dried over phosphorus pentoxide. Exhaustive extraction (Soxhlet) of the dry residue with ether (dried by distillation over sodium) gave fraction F_1 of ether-soluble sub-humic acids. The ether-insoluble material was dissolved in water and acidified by adding hydrochloric acid slightly in excess of the amount required to neutralize the remaining 45 per cent of the original sodium hydroxide. The mixture was now centrifuged to remove 'unchanged' humic acid, which was subsequently washed with water in the centrifuge and dried *in vacuo* over phosphorus pentoxide and sodium

hydroxide. It was not possible to remove all inorganic materials by washing, because freshly precipitated humic acid readily peptizes in solutions of low ionic strength. It was shown in later experiments that humic acids recovered as above usually contained about 20 to 25 per cent of inorganic material, so that the yields actually obtained corresponded to somewhat smaller amounts of the original humic acid.

The combined supernatant liquors and washings were evaporated to dryness and the residue dried *in vacuo* over phosphorus pentoxide and sodium hydroxide. Extraction (Soxhlet) with dry ether gave fraction F_2 of ether-soluble sub-humic acids, and subsequent extraction with acetone gave acetone-soluble acids. The F_1 fractions varied in colour from pale yellow to orange, while the F_2 fractions were brown. The acetone-soluble acids formed dark brown friable solids.

After the oxidation with 10 l. of oxygen the reaction mixture was acidified directly to precipitate the humic acid which was removed and the pale yellow liquor was then made alkaline with sodium hydroxide. A gelatinous red precipitate (probably ferric hydroxide) formed which on isolating and drying at 300°C weighed 0·738 g. This corresponded approximately with the ash (0·461 g) which could have been obtained from the original humic acid. The filtrate was re-acidified and evaporated; subsequent extraction yielded no ether-soluble acids and only a small amount of acetone-soluble material.

Ozonization of humic acid in the presence of excess alkali

The procedure used in these experiments was essentially the same as that described in the previous section, except that the samples of humic acid D 7 were dissolved in amounts of sodium hydroxide 2, 10 and 300 per cent in excess of the theoretical equivalent (value E_1). In each case 8 l. of oxygen was delivered from the reservoir; however, a small constant leak was later discovered between the oxygen pump and the ozonizer, and the volumes of oxygen consumed as ozone had therefore to be corrected by an amount which increased according to the time of reaction. The corrections were not large enough materially to affect the conclusions drawn from the results, which were also confirmed by carbon-balance ozonizations.

The reaction mixture from the first two oxidations, and from a corresponding oxidation using equivalent alkali, were all acid (pH 2 to 3). The oxidation with 300 per cent excess alkali gave an alkaline solution (pH 8). This solution was very much lighter in colour than the others. The working-up procedure was as previously described, the first addition of standard hydrochloric acid being equivalent to the excess of sodium hydroxide used plus 55 per cent of the theoretical equivalent of the humic acid.

The fraction F_1 ether-soluble acids from the first two oxidations were orange in colour, while those from the third were brown. On standing in a closed flask the acids from the oxidations using 10 and 300 per cent excess alkali evolved a brown gas, which dissolved in water to give an acid solution containing nitrate ion (brown ring test), and which was therefore nitrogen dioxide. In the experiment using 300 per cent excess of alkali the residue obtained after complete acidification gave a particularly copious evolution of

nitric oxide on drying *in vacuo*. This was shown strikingly by its conversion to brown nitrogen dioxide on admitting air to the vacuum desiccator.

The fraction F_2 ether-soluble acids were in each case darker than the corresponding F_1 acids. The acetone-soluble acids formed dark brown friable solids. The amount of organic material remaining unextracted by acetone was calculated by deducting from the weight of the insoluble residue the amount of sodium chloride corresponding to the sodium hydroxide used initially.

Carbon-balance ozonization of humic acid

For these experiments 10 g portions of humic acid D 355 were dissolved in 1, 1·5, 2 and 3 times the theoretical equivalent of alkali (calculated from value E_1) and ozonized using 8 l. of oxygen and a pumping speed of 20 l./h. Experience had already shown that the higher speed could safely be used without producing uncontrollable frothing in the reaction vessel. After each oxidation the distribution of carbon amongst the oxidation products was determined by the method described in detail in a previous paper[1]. All analyses were carried out in duplicate. The pH of each reaction solution was measured (B.D.H. Universal Indicator paper) and is shown in *Table 6*

Table 6. Yields and analyses of products from carbon-balance ozonizations

Item	*Amount of alkali*			
	Equivalent	1·5 × *equivalent*	2 × *equivalent*	3 × *equivalent*
pH *of reaction solution*	2	4	6	9
Wt of humic acid D 355 taken, g	10·006	10·006	10·006	10·007
Recovered humic acid:				
Yield, g	0·633	3·434	3·839	3·744
Carbon, %, d.a.f.	52·5	55·3	57·4	57·6
Hydrogen, %, d.a.f.	3·0	3·1	2·7	3·0
Ash, %	35·6	19·3	23·4	25·1
Sub-humic acids:				
Calculated yield, g, ash-free	9·26	5·91	4·96	5·07
Carbon, %, d.a.f.	28·1	30·6	28·5	25·5
Hydrogen, %, d.a.f.	3·1	4·1	4·6	4·3
Ash, %	38·5	48·3	55·3	64·7

together with the yields and analyses of the recovered humic acids and the sub-humic acids. A particular difficulty was experienced in semimicro combustion analysis of the sub-humic acids because of sampling errors due to the high inorganic salt content; this was overcome by dissolving the sub-humic acids in water and evaporating an aliquot portion directly in the combustion boat. The evaporation was quickly accomplished by placing the boat in a vacuum desiccator over phosphorus pentoxide. The yields of sub-humic acids are ash-free values, and are thus subject to some error because of possible changes in the inorganic substances during combustion.

Solubility of sodium humate

Samples (1 g) of humic acid D355 were dissolved in 1, 1·5 and 3 times the theoretical equivalent (value E_1) of sodium hydroxide, and the solutions were

diluted to 30 ml and shaken for 3 h. These procedures reproduced on a one-tenth scale those used in the ozonizations. The solutions were then centrifuged at 1 500 rev/min for 30 min and the supernatant liquors decanted. The residues were dried *in vacuo* over phosphorus pentoxide and weighed; the yields, multiplied tenfold, were respectively 90, 100 and 250 mg, and represented the maximum amount of sodium humate that could have been precipitated by the common ion effect at the start of the corresponding ozonizations.

Ozonization of recovered humic acid

The equivalent values E_1 and E_2 of humic acid D355 were measured by dissolving samples (about 80 mg) in 10 ml of 0·1N or 1·4N sodium hydroxide, allowing the solution to stand overnight in a carbon dioxide-free atmosphere, and back titrating potentiometrically (glass electrode) with 0·5N hydrochloric acid. The corresponding values were similarly determined for the humic acid recovered after the carbon-balance oxidation using 3 equivalents of alkali.

The recovered humic acid (3·5 g) was dissolved in equivalent (E_1) alkali and ozonized in the usual way using a pumping speed of 20 l./h. The frothing of the solution usually observed during shaking and during the early stages of ozonization was completely absent. Uptake of ozone was very slow, and only 200 ml of oxygen was absorbed in 48 h. Under these conditions 10 g of the original humic acid absorbs 8 l. of oxygen in about 20 h.

Grateful acknowledgement is made to Professor S. G. Ward of the Department of Mining, and to Drs A. C. Monkhouse and L. Horton of the Fuel Research Station, for their continued interest and helpful advice. The work forms part of the programme of the Fuel Research Board of the Department of Scientific and Industrial Research, and is published with the approval of the Director of Fuel Research.

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(*Received August 1958*)

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Recent Developments and Notes

FREIBERG COLLOQUIUM ON THE CHEMISTRY OF COAL

A colloquium on the chemistry of coal was held in the Bergakademie, Freiberg, on 12 and 13 April 1957, organized by the Brennstoff-technische Gesellschaft in der Deutschen Demokratischen Republik. The nine papers presented have now been published together with the discussions [*Freiberger Forschungsh.* A 80 (1958) 1–160]. The subjects dealt with include: the properties of pitch extracted from brown coal by pressure; a platinum–alumina catalyst in a dehydration plant; the effect of pre-treatment on the activity of oxide–sulphide mixed catalysts; the high pressure hydrogenation of Lauchhammer tar; the subsequent treatment of the primary products from the Fischer–Tropsch synthesis; the characterization of brown coals and the determination of the tar yield, especially in low-temperature carbonization; the chemical structure of coal.

MICROANALYSIS OF PETROLEUM

The amount of sample of oil available in the course of geological prospecting is frequently quite small and as complete an analysis as possible is required for commercial evaluation. A scheme for the analysis of a 5 ml sample of crude petroleum or its products has now been described by A. R. JAVES and C. LIDDELL, of the British Petroleum Co. Ltd, Research Station, Sunbury-on-Thames [*Analyt. Chem.* 30 (1958) 1570]. The sample of crude oil is distilled to yield four fractions with boiling points: (*i*) up to 149°C, (*ii*) 149° to 232°C, (*iii*) 232° to 371°C, (*iv*) 371° to 550°C. Methods are described for carrying out tests on the distillates and residues to determine specific gravity, aniline point, aromatic content, asphaltene content, bromine number, pour point, setting point, and viscosity. Some of these methods are based on I.P. or A.S.T.M. standard procedures, and others have been developed in the B.P. Analytical Research Laboratory.

It is found that these tests can be carried out on very small samples of petroleum products with little loss of accuracy. With due care, the results obtained on a 5 ml sample of crude oil agree sufficiently well with those from a 5 litre assay to give valuable evidence as to the type and origin of the oil.

AIR POLLUTION IN FRANCE

An Association for the Prevention of Atmospheric Pollution has recently been formed in France, with the cooperation of government, public health, fuel and power, and industrial interests. Professor BUGNARD, Director, Institut National d'Hygiène, is the president of the provisional governing board. The first objectives of the Association will be to define 'smokeless pilot towns' before the end of the year, to publish a journal, and to inaugurate information campaigns. A series of conferences is to be organized in 1959 in Paris.

AMERICAN STUDY OF AIR POLLUTION

In the summer and autumn of 1957 one of the most comprehensive studies of smoke and air pollution was conducted by the Interstate Sanitation Committee in the New York–New Jersey Metropolitan area. Atmospheric pollution in this area, affecting millions of people, has been a great and growing problem for many years. The project was planned and directed by Dr LOUIS C. MCCABE, and was carried out with the cooperation of the U.S. Public Health Service, the U.S. Weather Bureau, the U.S. Army Chemical Corps, and the U.S. Bureau of Standards. The report of this study has now been published, including guides for proposed legislation, entitled *Smoke and Air Pollution, New York–New Jersey* (Interstate Sanitation Commission: 10 Columbus Circle, New York 19, N.Y. February 1958).

Information was collected on: relationships of meteorology, visibility and pollution; interstate movement of pollution as indicated by releasing tracer dust in one state and collecting it in the other; amount of vehicle exhaust fumes and other organic materials in the air; sulphur dioxide and ozone concentration; effects of the polluted atmosphere on health, vegetation, materials and transportation; existing laws in the jurisdictions concerned.

HIGH-TEMPERATURE RESEARCH

In view of the current widespread interest in high-temperature research, the National Bureau of Standards has recently published a survey of this subject [*Tech. News Bull. U.S. Bur. Stand.* 42 (1958) 101 to 123 and 125 to 142]. The first part of this survey deals with the structure and properties of high-temperature materials, and the second part with high-temperature measurements.

In the temperature range from 2000° to 4000°C and above, there is a serious lack of basic scientific knowledge which prevents further advance in many scientific and technological fields. Above 1000°C very few usable data are available, at 2000° to 3000°C there is a serious lack, and at higher temperatures there are no data. Information is urgently needed on the thermodynamic properties of materials in solid, liquid and gaseous states over a very wide range of temperature, from 0° to 6000° or 8000°K, and over a pressure range from 1 to 10 000 atm. In heat and mass transfer and in fluid dynamic calculations, information is required on transport properties such as viscosity, thermal conductivity, and diffusion, at high temperatures. An increasing number of projects in the Bureau are now being extended into the high-temperature range. Reliable measurement techniques are needed in high-temperature research and the Bureau's present capability for routine calibration of high-temperature devices is limited to about 3000°C. It hopes to improve this by several thousand degrees in the next few years.

An *oscillating-cup* viscometer has been developed in the Bureau's laboratory to measure the viscosity of liquid inorganic oxides at temperatures up to 2000°C or higher. The sample liquid is enclosed in a cup that is suspended from a wire to form a torsion pendulum; and when torsional vibrations are started, the presence of the liquid causes them to be damped. As the amount of damping depends on the viscosity the latter can be calculated from the observed rate at which the vibrations decay.

During the past year a photoelectric pyrometer has been developed which uses the basic principles of the disappearing-filament optical pyrometer, but the brightness of the test body is compared with that of the pyrometer photoelectrically rather than visually. A substantial gain in precision is obtainable.

A recent addition to the Bureau's high-temperature research equipment is a solar furnace whereby small areas of materials can be raised to temperatures up to 3 500°C. This is being used for studies on the vaporization of refractory materials.

The Bureau is carrying out a programme of basic research on the physical and chemical processes occurring in flames and other high-temperature gases. Spectroscopic methods are used and the data obtained are proving useful in reaching a better understanding of combustion processes and also in the development of accurate spectroscopic methods for measuring high temperatures. In measuring flame temperatures spectroscopically, molecular distributions are calculated from observed spectral intensities and compared with distributions predicted theoretically for certain temperatures. The experimentally observed distribution may also be compared with distributions predicted theoretically for a range of equilibrium temperature values. If a certain temperature can be found that has a theoretical distribution agreeing with the observed one, then this is the temperature associated with the levels under study; or when the flame is substantially in equilibrium, this temperature is the temperature of the flame as a whole.

LIQUID FUELS CONFERENCE

The second liquid fuels conference now being arranged by the Institute of Fuel will be held in Torquay from 11 to 14 May 1959 and will be concerned with *Major Developments in Liquid Fuel Firing 1948–1959*. Eighteen papers have been set down for presentation and the subjects include: liquid fuels specifications and their significance; atomization and combustion of liquid fuel; design and performance of high momentum oil burners; physical properties of open-hearth furnace flames; pressure jet burners for boiler use; flow patterns as affecting furnace design; emissivity and radiation of steam- and air-atomized liquid fuel flames; operating conditions in shell boilers; packaged boilers; liquid fuel in the steel, metal, glass, and ceramics industries, and for domestic heating and the manufacture of town gas; works and power station boilers, and gas turbines.

Information about the conference may be obtained from the Institute of Fuel, 18 Devonshire Street, Portland Place, London, W.1.

AVIATION FUELLING SAFEGUARD

An automatic device known as the 'Fuel Monitor', designed to augment the present stringent precautions against contaminated fuel being fed into aircraft, has reached an advanced stage of development and field trials are now in progress. Solid contaminants in aviation fuels can effectively be removed by microfilters and water contamination can be avoided or detected with present-day equipment and techniques. There remains, however, the

possibility of failure of equipment or of the human element. There is, therefore, the need for an automatic monitoring device which would be both fully 'fail safe' and be situated as near to the end of the fuelling system and hence as close to the aircraft as possible.

The new monitor, which has been designed by The Shell Petroleum Co., in conjuction with Stream-Line Filters Ltd, of London, comprises a valve and sensitive element inserted in the main fuel stream to the aircraft. If contaminated fuel passes through the sensitive element the main valve closes. During normal operations the valve will open and close, as the delivery valve is opened and closed, so that it is repeatedly exercised and any risk of it becoming 'frozen' in the open position is eliminated.

In addition it is so constructed that faulty maintenance, such as failure to replace the element, will prevent the valve from opening. The element itself is robust and casual handling cannot cause damage. The complete unit can be installed easily on existing fuellers or hydrant dispensers.

OIL REFINERY PROJECT AT ALGIERS

The companies Beryl Algérie, Compagnie Française des Pétroles, Compagnie Française de Raffinage, Mobiloil Français, Société Française des Pétroles BP, Société Shell d'Algérie, and Standard Oil (New Jersey) have decided to form a new company with the object of constructing an oil refinery near Algiers, as soon as possible.

The refinery will be designed to treat Sahara crude oil and to produce all major products. The initial crude oil capacity of the refinery will be about two million tons a year. This will be sufficient to meet Algeria's oil product requirements which it is estimated will amount to one million tons per year at the time the refinery will come on stream.

WARREN SPRING LABORATORY

The Council for Scientific and Industrial Research has announced a change in the organization affecting the D.S.I.R. Warren Spring Laboratory, Stevenage. A Steering Committee has been set up to bear responsibility for the research programmes and this replaces the former Fuel Research Board. It is an essential feature of the new arrangement that the Steering Committee is a full committee of the Research Council and that there will be a direct link between the two bodies, because the Chairman of the Committee is a member of the Council.

In addition to the Chairman, Sir HARRY JEPHCOTT, who is also Chairman of the Research Council, there are four members of the Committee. Two are from industry, Dr R. HOLROYD, Deputy Chairman of Imperial Chemical Industries, and Mr D. A. OLIVER, C.B.E., Director of Research of the B.S.A. Group Research Centre. The other two members are Sir H. W. MELVILLE, F.R.S., Secretary of the Department of Scientific and Industrial Research and Mr S. H. CLARKE, C.B.E., Director of the Laboratory. The Committee is empowered to set up specialist sub-committees as necessary, to advise on the different fields of research covered by the Laboratory.

CALORIMETER FOR USE ON HIGH CALORIFIC GASES

The increasing use of gases with high calorific values such as butane, methane and refinery gases for supplementing the output of conventional plant has created many practical problems, amongst them the accurate determination of their calorific values.

As a result of work by The Gas Council at Watson House, London, a Fairweather calorimeter has been modified enabling it to be used on gases of calorific value from 420 to 4 600 B.Th.U./ft³ without altering the normal temperature rise or changing the recorder (apart from fitting different scales).

The modifications are of two general kinds, first, those to the escapement, water orifice and mercury switch to alter the range of the instrument, and secondly, the alterations made to the burner and combustion air system to give a satisfactory flame with different gases.

Practical tests with various possible methods of changing the water and gas rates on the Fairweather, showed that a combination of different water orifices with the 4/1 escapement was the simplest way of obtaining the required calorific value range. The double contact mercury switch, in combination with the 2/1 escapement and the different water orifices, was a satisfactory alternative and had the additional advantage that the change from a gas of 1 000 C.V. to a gas of 2 000 C.V. could be carried out almost instantaneously. Adjustment of the variable orifice setting is necessary after every change of range, as well as that of the rate of the independent primary air supply which is adopted.

SULPHUR IN TOWN GAS

Two papers were presented to the Annual General Meeting of the Institution of Gas Engineers in London in May 1958 dealing with sulphur in the utilization of town gas. In one of these, L. J. CLARK and E. SPIVEY, of the North Thames Gas Board, review in the light of the present day circumstances, the case for the further removal of the small amount of organic sulphur in gas which is destined for town supply [*Publ. Instn Gas Engrs, Lond., No. 523* (1958)]. It is shown that town gas of normal quality, when assessed on the standard of its performance in flueless appliances, is now markedly inferior to the best distillate oil and commercial liquefied petroleum gases. The ultimate limit of sulphur that is desirable is about 3 gr per 100 ft³ and a general reduction to 10 gr per 100 ft³ would represent an immediate advance that is possible. To achieve the latter reduction there are processes already in existence and those depending on the recovery of benzole have been well proved over a prolonged period. Removal of sulphur to the level of 5 gr per 100 ft³ and below can be attained by the active carbon process operating with a reduced adsorption period. The catalytic process may also produce a similar result and a combination of oil-washing or active carbon process with the catalytic process may very likely produce practically complete removal of sulphur. Sulphur removal will cost between 0·20 and 0·80*d* per therm of gas, depending on the method and extent of removal.

In the second paper, C. H. PURKIS, of Watson House, London, deals with sulphur and gas appliances [*Publ. Instn Gas Engrs, Lond., No. 524* (1958)]. Oxides

of sulphur formed by combustion are considered from the point of view of their physiological effects, mainly their smell and consequent influence on flueless space heating; of their physical effect on the dewpoint; and of their chemical effects in causing corrosion. These matters are considered in terms of safety, cost and prestige.

It is shown that the smell of sulphur oxides limits the use of gas for flueless space heating. The sulphur content would need to be reduced below 10, and preferably below 5 gr per 100 ft^3 before vitiation by carbon dioxide rather than smell became the limiting factor in installation. Corrosion by acid condensate affects the design and involves regular maintenance of balanced-flue space heaters and air heaters. Non-condensing instantaneous water heaters constructed of copper and protected by a lead–tin alloy, are corroded by sulphur oxides and thereby may become dangerous in use. It is considered by the author that if the intended expansion of domestic gas utilization in the space- and water-heating fields is to be a major objective of gas industry policy, sulphur reduction must be a matter of high priority.

THERMAL INSULATION OF INDUSTRIAL BUILDINGS

The Minister of Power has now made Regulations under the Thermal Insulation (Industrial Buildings) Act, 1957 [see *Fuel, Lond.* 37 (1958) 343], prescribing a standard of insulation against the loss of heat from the roofs of new industrial buildings or extensions begun on or after 1 January 1959. Some classes of buildings are exempted.

The standard of insulation has been chosen as that which, over industry as a whole, will secure worthwhile fuel savings at reasonable cost. It can readily be achieved using materials and constructions widely available. In most new industrial buildings it is now generally accepted that the additional cost of insulation is offset in three or four years by the savings in fuel costs alone, and on these grounds it may be more profitable in some buildings to aim at a better standard of insulation than that prescribed.

The Regulations [The Thermal Insulation (Industrial Buildings) Regulations 1958 (*S.I. No. 1220/1958*)] also specify the kinds of materials which, if used to a substantial extent to achieve the standard of insulation, must either conform to a prescribed standard of resistance to the spread of flame or be used in such a way that they do not add to the risk of fire.

An *Explanatory Memorandum* (Her Majesty's Stationery Office: London, 1958) for the technical guidance of those concerned in the administration and operation of the Act and Regulations has been published.

GERMANIUM IN AUSTRALIAN COAL

Consequent upon the discovery in the past fifteen years or so of the unusual electrical properties of germanium, leading to its use in the electronics industry, search has been made to find sources suitable for its economic recovery. The presence of germanium in coal was first established over twenty five years ago by V. M. GOLDSCHMIDT, who showed that it is frequently present in ash from coal in higher concentrations than the average in the earth's crust. In the past few years many papers have been published on

the distribution and mode of occurrence of this element in coal deposits throughout the world.

In 1953 the Coal Research Section of the Commonwealth Scientific and Industrial Research Organization began a survey of the occurrence of germanium in Australian coals and a report on this work has now been published by R. A. DURIE and H. N. S. SCHAFER (Reference *T.C. 27*; September 1958). Up to date analyses have been made of 270 samples from 22 coal seams. The germanium content of the ashes from the majority of these coals is between 0·001 and 0·003 per cent. The highest contents have been found in coals from the Burragorang Valley area of the Bulli seam where a seam subsection yielded an ash with 0·06 per cent of germanium, 0·1 per cent being the minimum concentration necessary for present-day economic recovery from ash and flue dusts. In Australian coals the germanium does not appear to be preferentially associated with the coal substance as it is in some coals in other parts of the world.

NUCLEAR PROCESSING OF PETROLEUM

Esso Research and Engineering Co. announce that nuclear reactors can now be used to process petroleum and chemicals in commercial quantities [*Inst. Petrol. Rev.* 12 (1958) 353]. The progress in adapting atomic energy to oil refining was reported by F. T. BARR, H. J. OGORZALY and T. A. REITER in a paper presented to the International Conference on Peaceful Uses of Atomic Energy 1958.

There are three major radiation sources available, radio-isotopes, electron accelerators, and nuclear reactors. Each source is used so as to take advantage of its special properties. The nuclear reactor provides the cheapest radiation, but operates economically only in large capacities. A specially designed reactor can be applied to radiation processing by passing the liquid process material, for instance a petroleum cut, directly through the core where the energy of the atomic reaction is being released. In their paper, the Esso Research team indicate that, at a refining cost of only a few cents per gallon, radiation may be able to reduce the pressure and temperatures needed in petroleum refining, augment the effectiveness of, or, replace catalysts and improve the quality of oil products.

NEW METHOD FOR DETERMINING VAPOUR PRESSURE

The Reid method has been the standard one for many years of measuring the vapour pressure of petroleum products, but this has poor reproducibility and has resulted in much unnecessary expense in refineries. A new method, known as the Micro Vapour Pressure Method (MVP) has been developed by Esso Research and Engineering Co., U.S.A., and is claimed to have five times the precision of the Reid method. A determination can be made in 10 min instead of the 45 min required for the Reid method and MVP results can be correlated directly with Reid results. In the new apparatus the sample of liquid is introduced into an evacuated bulb, measurements of vapour pressure being made before and after introduction of the sample. The greater precision obtainable in this way will be reflected in the increased accuracy of gasoline blending [*Inst. Petrol. Rev.* 12 (1958) 315].

DECREPITATION OF ANTHRACITE

The physical instability or decrepitation of anthracite due to thermal shock and its consequent mechanical weakness, are well known although they have not been much studied. These features preclude the use of raw anthracite for some industrial purposes, for example, in shaft furnaces. In the past few years, however, attention has been directed to the problem of using anthracite in certain operations instead of metallurgical coke, particularly in America and Russia, which are producers of large amounts of anthracite. A recent paper on the subject by L. DELVAUX, of the University of Liège, and R. J. GRACE, of Bituminous Coal Research, Inc., Columbus, U.S.A., describes an investigation into the causes of decrepitation and the possibility of its reduction to enable anthracite to be used in cupola furnaces [*Chim. et Industr.* 79 (1958) 579].

Four Pennsylvanian anthracites were studied, 92 to 96 per cent carbon content d.m.f. The samples were heated in a gas-fired muffle, in a controlled reducing atmosphere, up to various temperatures at different rates and measurements were made of the index of friability and the index of volatile matter as functions of the rate of heating and of the temperature of carbonization, for samples of different sizes, 8 to 14, 14 to 22, 60 to 80 mm. The friability index was obtained by submitting the carbonized product to a modified form of the shatter test.

It is concluded that there are three distinct temperature ranges concerned with the decrepitation of anthracite, below 550°C, between 550° and 850°C, and above 850°C, and the amount of volatile matter released and the rate of release are of fundamental importance in this connection. The release of volatile matter is accompanied not only by macroscopic effects such as internal pressure, but from X-ray analysis it appears that there are also microscopic effects concerned with the internal structure of the crystallites. By means of suitable thermal treatment for stabilization, certain types of anthracite may be rendered usable for metallurgical purposes.

U.S.A. COAL AND ELECTRIC UTILITIES RESEARCH PROJECTS

In the current issue of *Bituminous Coal Research* [18 (No. 3, 1958) 3] it is reported that American electric utility and coal industries have combined to finance a major research programme. The programme is being sponsored by the Association of Edison Illuminating Companies and Edison Electric Institute, representing the investor-owned electric utility companies, and Bituminous Coal Research, Inc., representing the coal industry. This cooperative effort reflects the realization by these two major industries of a long-range mutual interest.

The projects, which are being planned for a two-year period, will be undertaken at the laboratories of B.C.R., Inc. One of the problems to be studied immediately is the reduction of sulphur dioxide and other contaminants in flue gas as produced and the reduction of sulphur in steam coals prior to burning. As is well known, methods at present available for removing contaminants from flue gas are economically or otherwise unattractive.

WORLD POWER CONFERENCE

During the Canadian Sectional Meeting of the World Power Conference, held in Montreal, 7 to 11 September 1958, the International Executive Council presided over by Sir VINCENT DE FERRANTI, considered the arrangements for future conferences. The next Sectional Meeting will be held in Madrid, the dates tentatively selected being 5 to 9 June 1960. The Sixth (Plenary) World Power Conference will take place in Melbourne in October 1962. The Sectional Meeting after that will be held in Switzerland in 1964. The next meeting of the International Executive Council will be held at Rome in June 1959, by invitation of the Italian National Committee.

A.S.T.M. STANDARDS ON GASEOUS FUELS D–3

A new compilation of American standards on gaseous fuels has recently been issued and replaces the edition published in 1954. It contains four methods for sampling and measurement and nine methods of testing and analysis. Of these, seven are new, revised, or have had their status changed since the last edition was published. Natural gas, manufactured gas, and liquefied petroleum gases are materials for which these standards have been specifically written.

Copies of this publication may be obtained from the American Society for Testing Materials, 1916 Race Street, Philadelphia 3, Pa, at $3.00 per copy.

U.S.A. NATIONAL FIRE CODES

Important changes in fire safety standards in the United States of America are incorporated in a new and revised edition of the *National Fire Codes* recently published by the National Fire Protection Association.

The 1958 edition consists of six volumes and is a compilation of the 170 standards developed by the N.F.P.A. in the fields of inflammable liquids and gases, combustible solids, dusts, chemicals and explosives, building construction and equipment, extinguishing equipment, electrical, transportation and miscellaneous operations.

New material in the 1958 edition includes 38 new or revised fire safety standards adopted at the 1958 N.F.P.A. Annual Meeting. It also incorporates all amendments approved by the N.F.P.A. Board of Directors up to and including 30 July 1958.

Purely advisory so far as the National Fire Protection Association is concerned, the codes are used widely in the United States, Canada and abroad by property owners, legal and insurance interests, and others responsible in the field of fire safety.

The *National Fire Codes*, $7.00 per volume, may be obtained from the Publications Department, National Fire Protection Association, 60 Batterymarch Street, Boston 10, Massachesetts.

SEPARATION OF AIRBORNE PARTICLES

The separation of the fine constituents from a polydisperse system may cause a change in the composition of these constituents. Therefore investigations regarding the structure and behaviour of suspensions having predominantly fine constituents require separation methods which do not affect the physical

and chemical characteristics of the suspended particles. According to A. GOETZ this requirement is satisfied by centrifugal separation and he has described an instrument for the quantitative separation and size-classification of airborne particulate matter down to 0·2 micron in size [*Geofis. pur. appl.* 36 (1957) 49; abstract in *Appl. Mech. Rev.* 11 (1958) 518]. High centrifugal accelerations permit the separation of particles down to about 2 microns (at density = 1·0) but they fail below this particle size owing to the smallness of the impulse of these small particles, a consequence of their small mass, which prevents them from penetrating the boundary layer adhering to the channel wall. This difficulty is removed by giving the helical channels, through which the air stream flows, a rotation in the same sense as the air flow. Thereby high centrifugal accelerations can be attained even at laminar flow conditions, and the radial movement of the particles is facilitated. The factors determining the particle path are: radius and angular velocity of the helical channel, radial width of the channel, and relative velocity between air and channel. If the channel walls are built removable then the separated aerosol can be collected. The author discusses the relation between the design data of the instrument and its performance characteristics, and gives a detailed description of the first experimental unit. Examples of five monodisperse aerosols, ranging between 1·19 and 0·19 micron, are given.

MAGNETOCHEMISTRY OF PETROLEUM

A paper by H. HONDA, of the Natural Resources Research Institute, Japan, on relations between the magnetic susceptibilities of hydrocarbons and a number of physical constants was published about five years ago and has recently been translated for the Branch of Bituminous Coal Research, U.S. Bureau of Mines [*J. Fuel Soc. Japan*, 32 (316) (1953) 447 to 460].

About fifty years ago M. P. PASCAL measured the diamagnetism of many organic compounds and found an additive relationship in that the molecular magnetic susceptibility can be approximately expressed by the sum of the susceptibilities of the component atoms and, when necessary, a structural term. Since that time a very large number of magnetic susceptibilities of hydrocarbons have been measured, particularly by S. BROERSMA [*J. chem. Phys.* 17 (1949) 873]. Using these values the present author has sought relationships between them and the number of carbon atoms, specific gravity, molecular weight, molecular volume, refractive index, molecular refraction, and boiling point. The magnetic correlation index, *MI*, was obtained from the volume magnetic susceptibility of a hydrocarbon and its specific gravity, and from the *MI* value the series to which the hydrocarbon belonged could be determined. It was then possible to determine the molecular volume, refractive index, molecular refraction, and boiling point from the magnetic susceptibility value. Unmeasurable physical constants which may be determined by these relationships from the magnetic susceptibility values should prove useful in the study of petroleum.

GAS IN EUROPE

The Commission for Energy, appointed by the Council of the Organization for European Economic Cooperation (O.E.E.C.) and constituted in 1955,

recommended the formation of a Gas Committee as a fourth committee in the Energy Sector in addition to the already existing Coal, Oil and Electricity Committees. The Gas Committee was established at the beginning of 1956 and has recently issued its first report *Gas in Europe: Production, Availabilities, Consumption* [O.E.E.C: Paris, August 1958]. The problems studied include production, transport, distribution and utilization of gas, with the exception of questions of production of natural and refinery gas. The report covers the period 1954 to 1956 and makes certain forecasts for the period up to 1960.

Because of the complexity and diversity of gas sources, their interdependence and interlinking, and the different problems related to each of these sources, this first report is limited to a survey of the gas sector in sixteen individual member countries.

SUPERCRITICAL PRESSURES IN STEAM POWER PLANTS

At the Canadian Sectional Meeting of the World Power Conference at Montreal in September 1958, a paper was read by P. PROFOS, of Winterthur, on the impact of supercritical pressures on the economy of steam power stations. Investigations were carried out jointly by two Swiss mechanical engineering companies to ascertain the optimum efficiency from the economic point of view, as a function of the limiting thermodynamic parameters, and particularly the pressure.

A comparison of three projects was made, the output in each was 250 MW at maximum continuous load and 230 MW at economical load. One of the plants was for high subcritical pressure, one for supercritical pressure and one for the same supercritical live-steam pressure but with double reheat. The turbine inlet pressures were respectively 2 503 and 4 351 lb/in^2. The live-steam temperature was taken as 565°C for the subcritical cycle and as 600°C for the other two projects. The reheat temperature was fixed at 565°C for all three projects.

The calculated plant efficiencies were based on the net calorific value of the coal and on the net output of the turbine generator. There is found to be an improvement in efficiency of 2·74 per cent by changing from subcritical to supercritical pressure, and the adoption of double reheat results in the efficiency being raised further, by about 1·47 per cent. These improvements in efficiency must be considered in conjunction with the increased outlay for the plant and a judgment as to how far the improvements are economically justified can only be made on the basis of an overall economy balance.

FUEL IN U.S.S.R. OIL REFINERIES

D. A. TARASOV and I. I. TATARINOV, in a paper read to the Canadian Sectional Meeting of the World Power Conference held at Montreal in September 1958, reviewed the measures directed during the past ten years or so to improving the utilization of fuels burnt by oil refineries in the U.S.S.R. The oil industry is one of the main users of fuel in the Soviet Union, and on a calorific basis the consumption of fuel of all kinds in the industry directly and also indirectly in the form of electric heat and power, amounts to about 17 per cent of the

overall production of oil and associated gas. In the past five years or so the proportion of fuel directly consumed has diminished from about 81 per cent to 73 per cent due to the increasing trend to use more of the centralized supplies of heat and power. The share of indirect fuel burnt, however, was slightly reduced during this period owing to a considerable reduction of fuel consumption per unit of electric power produced by the generating stations of the power supply grids.

A description is given of methods practised in the U.S.S.R. oil refineries to improve the efficiency of fuel consumption. The supply of oil refineries with heat and power from high-pressure (100 atm, 540°C) centralized power stations, designed for the combined production of electricity and steam, has reduced the total fuel consumption of newly built refineries by 5 per cent as compared with pre-1939 values. The utilization of exhaust steam and the substitution of electrically driven pumps for steam driven ones has reduced the total fuel used by about 10 per cent, and the utilization of hot oil products and superheated water in heat exchangers and in other ways has brought about a reduction of 6 per cent in fuel used. The collection and return of steam condensate to the centralized heat supply generating stations and the use of oil processing plants of larger capacity reduce the fuel consumption respectively by 2·5 and 10 per cent. With processing plants of larger capacity, say 2 to 3 million tons of oil for primary treatment per annum, reduction in the amount of fuel used is mainly due to shortening of the refinery lines of communication and to the consequent decrease of the cooling surfaces of processing apparatus and reservoirs.

A new type of furnace has been developed by the Giproneftemash State Designing Institute. A special feature of this furnace is that it is provided with a firebox having radiating walls made up of panel burners and double-sided radiation screen. By this means the furnace efficiency is increased by 10 to 15 per cent and the cost of construction of such furnaces is less than half that of the usual type for the same capacity.

Two new types of air-heaters for the tubular furnaces are described, one with recirculation of a portion of the air warmed within the heater, and the resulting saving in fuel is assessed at 6 per cent.

FUEL DEVELOPMENTS IN JAPAN

The development of fluidization processes for carbonization and gasification of coal in Japan was described by A. BABA, Director of the Resources Research Institute, Japan, in a paper presented to the Canadian Sectional Meeting of the World Power Conference at Montreal in September 1958. Investigations have been proceeding in the past few years in the Resources Research Institute, the Coal Research Institute, and in some large industrial organizations, on the best means of carbonizing and gasifying indigenous low grade coal, and particular attention has been given to fluidization processes.

A fluidized carbonization process using internal heating is described. The temperature of carbonization is 500° to 600°C. The char obtained from an industrial plant is used for the manufacture of domestic briquettes, and the gas and tar for steam raising. Another process has been developed in which

the objective is to obtain a gas of higher calorific value, at least 3 600 kcal per m^3 (gross), which is the standard of town gas in Japan. For this purpose external as well as internal heating is used, and the temperature of carbonization is 700° to 800°C. A full-scale industrial project using this process is now under consideration. Data are given that show the economic advantage of both fluidized carbonization and gasification processes over conventional methods.

SEVENTH COAL SCIENCE LECTURE

The British Coal Utilisation Research Association's Seventh Coal Science Lecture was delivered at the Institution of Civil Engineers, London, on 15 October by Sir CHARLES GOODEVE, O.B.E., D.Sc., F.R.S., Director of the British Iron and Steel Research Association, who took as his subject 'Carbon: the key to metallurgy'.

The theme was introduced by reference to the remarkable role played by carbon in the history of extraction metallurgy since prehistoric times. With few exceptions, the commercial production of most of the important chemical elements depends today on the use of carbon to reduce an oxide or some other compound containing oxygen in combination.

Besides its function as a 'universal key' carbon plays two other important roles in extraction metallurgy. One is its ceramic function of which the manufacture of uranium is a good example; the other is the ability of carbon to impart greater strength to metals and steel is the outstanding example here.

The explanation of carbon's remarkable properties as a 'key' element in releasing elements from their compounds with oxygen lies ultimately in the fact that when it is oxidized to form carbon monoxide the reaction is accompanied by an *increase* in gas volume and therefore in entropy, that is, an increase in the 'disorder' of the chemical system. The free energy change in the reaction between carbon and oxygen becomes, therefore, more negative at high temperature. On the other hand, the free energy change for metal–oxygen reactions becomes less negative at high temperature. Consequently, if the temperature is high enough the net free energy of reduction by carbon becomes negative and oxygen can be removed from any ore to combine with carbon as carbon monoxide, leaving the metal.

Another advantage possessed by carbon is that in its various forms it provides a wide choice of reactivities. The ability to choose the best degree of activity for a particular purpose is of great value, especially in the blast furnace, and in the preparation of ores for smelting where the reactivity of the coke is a key factor in the success of the operation.

Carbon's unique position in extraction metallurgy is not likely to be seriously challenged within the foreseeable future. The nearest rival is hydrogen, but there are many practical difficulties in preparing and keeping hydrogen dry enough for the purpose.

The increase in the use of 'tonnage' oxygen, which is having profound effects on the refining of metals, can increase the usefulness of coal. Nuclear energy will probably have its greatest impact upon metallurgy through the cheapening

of electricity. Carbon can thus be expected to retain its dominant position, and Great Britain's large reserves of coking coals would provide industrial security for many years yet.

After the Lecture a dinner in honour of Sir CHARLES GOODEVE was held at the Savoy Hotel and at this function the Coal Science Medal was presented to him by the President of the B.C.U.R.A., Dr W. IDRIS JONES, C.B.E.

MOLECULAR SIEVES IN THE PETROLEUM INDUSTRY

One of the latest uses to be reported for molecular sieves is that of the removal of sulphur and water from sour natural gas and refinery gases [*Chem. Engng*, 65 (No. 21, 1958) 66]. A dual-bed process, with a single-pass, is used and a reduction, for example, from 73 gr H_2S per 100 ft^3 of natural gas to 0·025 gr is possible, with dewpoints approaching − 100°F. The cost is below that for multistage processes such as that using monoethanolamine scrubbers followed by a drying column.

Molecular sieves are being increasingly used in drying refinery process gases. They are used, to the extent of about 5 per cent of the total desiccant weight, to back up less costly drying agents such as alumina and silica gel, so as to give greater overall capacity and much lower dewpoints. A thin layer, or trimmer bed, of molecular sieves is used in the drying tower outlet, after the main drying load has been handled by the cheaper material.

It was also announced recently that the sieves are being used by the Texas Co. in a pilot plant to separate *normal* and *iso* paraffins. The process is said to be now commercially feasible and its importance is in the ability to remove easily the low-octane-number *normal* paraffins from naphtha or reformate and also in the reduced amount of alkylate which is consequently needed for gasoline blending stock.

PIPELINE GAS FROM OIL SHALE

An exploratory investigation has been made in the Institute of Gas Technology, Chicago, of the high pressure hydrogenolysis of oil shale as part of a general programme concerned with the production from liquid and solid fossil fuels of fuel which might prove to be a supplement to, or substitute for, natural gas. The work is being undertaken in view of the recently indicated need in the U.S.A. for the development of economic methods for the production of pipeline gas from a material such as shale, of which there are large reserves in the continent. The preliminary work was described by E. B. SHULZ Jr and H. R. LINDEN in a paper presented to the Division of Gas and Fuel Chemistry of the American Chemical Society, at its Illinois meeting, 7 to 12 September 1958. The immediate objective of this work was to determine if the recovery of the organic constituents of oil shale in the form of gas of high heating value would provide an attractive alternative to the conventional approach of processing oil shale with a view to obtaining the maximum recovery of liquid products.

A typical Colorado oil shale was submitted to batch hydrogenolysis at a maximum reactor temperature of 700°C, and maximum pressures of 1 200

to 5 700 lb/in² gauge. The hydrogen/shale ratios used were equivalent to 50 to 200 per cent of the stoichiometric requirements for the complete conversion of the organic carbon plus hydrogen content to methane.

Nearly complete conversion of the organic matter in the shale to a fuel gas with high methane and ethane contents was obtained, the heating value being over 800 B.Th.U./ft³, and there was only little formation of oxides of carbon from mineral carbonate decomposition. A relatively short residence time in the reactor is required and it is not necessary to reduce the shale to very small size as quite insignificant effects on gas yields and composition were found from a variation in particle size range from 5–20 mesh to 140–325 mesh. In view of the relatively low material costs, the results are said to indicate that serious consideration should be given to supplementing the future supply of natural gas with synthetic gas of high heating value from oil shale, particularly in areas served by long distance transmission lines passing in the vicinity of the Colorado deposits.

SIZE DISTRIBUTION OF BROKEN COAL

A new theory of the size distribution of broken coal was put forward in a paper by I. EVANS, of the Mining Research Establishment, National Coal Board, Isleworth, Middlesex, at the Institute of Fuel Conference on 'Science in the Use of Coal', held in Sheffield, April 1958. The author reviews the more important suggestions which have been made to express size distribution of materials that have been fragmented in various ways. The Rosin–Rammler relationship has gained wide acceptance and an expression of the same type was formulated some years ago by J. G. BENNETT and others [*J. Inst. Fuel*, 10 (1936) 22; 14 (1941) 111] as the 'ideal law of breakage', taking into account only the distribution of weaknesses and disregarding the other factor in the breakage of coal, the distribution of stress.

The present author considers that Bennett's assumptions will not lead to a satisfactory size distribution law, and the Rosin–Rammler expression may have no fundamental validity. His new approach is derived from a consideration of work on the strength of cubes of coal in uniaxial compression carried out by himself and C. D. POMEROY. From this work a fundamental relation is found governing statistical considerations of strength. The equation expressing this relationship is an example of the 'weakest-link' theory of breakage. The application of the theory to the breakage of coal is said by the author to lie in terms of the propagation under tensile stress of cracks contained in the coal, the extension of the 'weakest' crack (that is, the one which propagates under the least stress) initiating a chain of breakage throughout the specimen.

In the mathematical treatment of the subject, the size distribution deduced, in the form of percentage by weight undersize against size, is recognizable as the incomplete gamma function. This function has previously been suggested on empirical grounds, as having applicability to size distribution curves. The function is shown to be a good fit to observed size distribution and the Rosin–Rammler empirical equation is related to the function.

W. A. KIRKBY

COMBUSTION AND FLAME

Readers of *Fuel* may like to know that the following *Notes* appeared in the December issue of *Combustion and Flame*:

Vortex furnace
Brown coal as turbine fuel
The carbon monoxide boiler
Motor exhaust gases

Obituary
Dr Marie Stopes

DR MARIE STOPES, who died on 2 October 1958 at the age of 78 at her home, Norbury Park near Dorking, was a woman of remarkable character and attainments. This is not the place to discuss the pioneer work on birth control which made her famous and notorious and which has been said to have transformed the thoughts of her generation about the physical aspects of marriage and the role of contraception in married life. The interest of readers of *Fuel* will lie in her contributions to the knowledge of the constitution of coal.

MARIE CARMICHAEL STOPES was born in Edinburgh, the first child of HENRY STOPES, a professional architect, a collector of fossils and prehistoric stone implements, and a judge of malting barley. Her mother, CHARLOTTE CARMICHAEL, was a pioneer of women's university education and the author of books on Shakespearean contemporary history. Thus, MARIE inherited from her parents both an interest in scientific inquiry and literary abilities.

She attended school first in Edinburgh and later in Hampstead. She studied botany under Professor OLIVER at University College, London, followed by a year under GOEBEL at Munich, where she graduated as Ph.D. On returning to London she devoted herself to palaeobotany, took her D.Sc. degree and secured in 1904 a lectureship at Owens College, Manchester University, on the recommendation of Sir WILLIAM BOYD DAWKINS. In 1907 she went to Japan where she spent nearly two years at Tokyo University and collected fossil plants later described in several memoirs.

On her return from Japan, Dr STOPES contracted a marriage in Canada which proved unhappy and was annulled. Back in Manchester, her interest in the geology and palaeontology of coal was aroused. Among many papers during the following period that by STOPES and WATSON on 'Coal balls' may be mentioned.

Having rejoined the staff of University College, London, she married in 1918 HUMPHREY VERDON ROE. There were two sons of the marriage, the elder of whom died soon after birth.

It was then that her main contribution to coal research took shape. In 1918 the *Monograph on the Constitution of Coal* by STOPES and R. V. WHEELER appeared. It was a well documented critical survey of the relevant literature up to that time. In the following year MARIE STOPES published [*Proc. Roy. Soc. B* 90 (1919) 470] her well known paper 'On the four visible ingredients in banded bituminous coal—Studies in the composition of coal No. 1'. The recognition by ocular inspection of these four distinct portions, separated with a pocket knife from hand picked specimens, proved fruitful. It greatly influenced subsequent coal research, particularly after the characteristic

differences between these 'rock types' and their relevance to practical problems had been established by coking tests and ash analyses carried out by the chemists among her friends. The differentiation was adopted in principle by many coal researchers in Europe, but any modifications of detail suggested by others roused her dynamic temperament to vehement protests. As she had invented and defended a sex language of her own, so she resisted any tampering with her nomenclature of coal constituents.

Dr STOPES reluctantly accepted the use by German workers of the ending -it in place of -ain of her own notation, vit*rain*, clar*ain*, dur*ain*, words which she had coined in line with fus*ain*, previously named by the French. But she would never forgive R. THIESSEN and his colleagues for adhering to the terms anthraxylon and attritus, though she recognized the differences between American and European coals.

Her unquenchable urge to coin words found final expression in 'A classification of coal ingredients' [*Fuel, Lond.* 14 (1935) 4–13]. This ambitious scheme for defining, naming and grouping a great number of mummified or mineralized plant entities, called macerals, received after lengthy discussions the blessing of workers in this field, notably those members of the Coal Research Club most concerned with coal classification, and has found a limited adoption.

This paper was the swan song of MARIE STOPES on coal research. Her subsequent interest in the subject may be aptly described by the title of one of her many books in another sphere as *Enduring Passion*.

The actions of this woman of outstanding intellect were often and greatly influenced by emotion. She was said by one of her biographers to be 'sometimes so completely under the power of her own self-persuading eloquence that her critical faculty was for the moment arrested'. For example, she danced with joy when her hope that one of the four ingredients might yield a coke button of a mushroom shape was gratified, vitrain coke turning out in that form. Her dogmatism, which allowed no argument, could turn to active dislike of those not in complete agreement with her and even of friends and co-workers who tried to hold the balance fairly between contending parties.

Although MARIE STOPES was the subject of much criticism, her name is firmly established in the literature on the constitution of coal and the names of her 'ingredients' have even found a place in the popular dictionaries.

R. LESSING

OVERSEAS CORRESPONDENTS' NOTES

The Editor is grateful for the following information on matters of present interest relating to the fuel science field. Monsieur R. Cheradame has kindly supplied the notes on France, while those on Germany were contributed by Dr W. Gumz, those on South Africa by Dr A. J. Petrick, and those on The Netherlands by Professor D. W. van Krevelen.

FRANCE

Congresses and conferences

THE 75th Congress of the Gas Industry, organized by l'Association Technique du Gaz en France, was held during 23 to 28 June 1958 in Paris. The 76th Congress will take place during the last week of June 1959 at Aix-les-Bains (Savoie).

The third one-day study on 'Flames' took place on 28 February in Paris; the fourth will be held in 1960.

The 'International Meetings on Heating, Ventilation and Air Conditioning', organized by l'Institut Technique du Bâtiment et des Travaux Publics, will take place during 25 to 27 May 1959 in Paris.

Coke ovens

During the first nine months of 1958, 235 coke ovens to produce 3180 tons of coke per day were brought into service.

Processing of by-products

Brought into service—In December 1957 a 360 ton/day unit for treating tar was started up at the Usines de Marienau (Moselle), and in February 1958 a 40 ton/day unit commenced manufacture of pure naphthalene for the same concern.

Work at the CERCHAR

Briquetting—The principal objective is still the reduction of tar consumption by:

(*1*) improving average production by perfecting the automatic regulation of existing machines

(*2*) the utilization of bitumen

(*3*) using the 'fluxing of the binder' technique.

Coal structure—Research has followed the directions listed:

(*1*) Manner of association of the elementary petrographic constituents of coal

(*2*) Micellar organization of organic matter (x-ray diffraction at small angles, specific surface, adsorption phenomena)

(*3*) Arrangement of carbon atoms, studied by x-ray diffraction

(*4*) Microporosity

(*5*) Study of chemical structure by controlled degradation: pyrolysis, hydrogenation.

Carbonization—An analysis of the factors that determine the behaviour of coke in a cupola furnace and especially the reactivity of coke with respect to carbon dioxide is being pursued in conjunction with le Centre de la Fonderie.

At the Marienau Experimental Station, the CERCHAR is carrying out in cooperation with the IRSID a study on the influence of the different factors defining coking blends on the quality of the coke obtained in ovens on an industrial scale. The process for manufacture of semi-coke or coke dust by fluidization has been completed.

GERMANY

A centenary in the mining industry

ONE of the most noteworthy events in the fuel field 1958 in Germany was the centenary of the *Bergbauverein* (Mining Association). It was organized in 1858 under the somewhat particularized name of *Verein für die bergbaulichen Interessen im Oberbergamtsbezirk Dortmund*—for short *Bergbau-Verein*—in Essen. At that time the need for such an association was strongly felt by coal producers because of a serious crisis in the coal market, and those 100 years of *Bergbau-Verein* coincide with the rapid industrialization of Germany and the full expansion of the coal-producing industry from about 4 million tons in 1858 to over 120 million tons 100 years later.

This year's *Steinkohlentag*, the annual event of the bituminous coal industry, was intended as a celebration of this centenary, although the present unfavourable market situation for coal in Germany as well as more generally has somewhat dimmed the festive mood. A review of a century of development in the coal industry, especially on the Ruhr, was given in a technical survey by Professor FRIEDENSBURG, and in an economic survey by Professor WESSELS. This period has not only seen a steady increase of production, of the capacity of individual mines, of the working depth, the step from drift mining to deep mining, the expansion of the so-called Ruhr area from the valley of the Ruhr up north to those of Emscher and Lippe; it has also brought about the advent of coal preparation, of by-product coke production, of the development of a far-reaching gas grid and many other new technical features. A *History of Coking Techniques* has recently been edited by *Steinkohlenbergbauverein* as a contribution to and an elucidation of this rapidly growing industry*.

Originally the *Verein* was mostly concerned with problems of legislation and jurisdiction, marketing, traffic regulations, labour, economy, and public relations, technical problems of common interest, and the exchange of experiences. Since 1919, however, new developments have played a role of ever-increasing importance, a trend which started at the beginning of this century—until the reorganized *Steinkohlenbergbauverein* (1953) became an exclusively technical and research organization for the entire West German coal industry. The other problems mentioned are handled by the sister organization, *Unternehmensverband Ruhrbergbau*.

* F. M. RESS, *Geschichte der Kokereitechnik*. Glückauf-Verlag: Essen, 1957.

Preceding this centenary was the Mining Exhibition 1958 in Essen, since 1945 a bi-annual show of the mining and mining equipment industries.

Immediately following the *Steinkohlentag*, the new Mining Research Centre (*Bergbau-Forschungsanstalt**) at Essen-Kray was opened. It comprises a chemistry, physics, and administration building together with three special buildings for pilot plant experimentation, and a mine ventilation research station. It centralizes the various activities of existing laboratories formerly spread over the whole Ruhr area from Essen to Dortmund in somewhat inadequate cramped quarters and offers good opportunities for further research and development. The plans for erecting such a research station were first mooted twenty years ago, but the final decision was taken only about three years ago at a time of a favourable state of the coal market. The first section of the Centre was completed at a time when an economic recession coincided with a structural change in the field of energy production, caused by competitive sources of energy, mainly oil, but in some countries including also natural gas, with atomic energy as a potential competitor in the future. In the face of such a predicament, expanded research and better research facilities are not only fully justified but a pre-requisite for the coal industry's survival. A new phase in German coal mining and coal utilization research has just begun.

SOUTH AFRICA

Increased production of oil from coal

The Minister of Economic Affairs, Dr VAN RHIJN, told Parliament that in its first year (between August and December 1955) the SASOL plant (oil from coal) produced 321 969 gallons of petrol and other fuels, including liquefied petroleum gas, compared with 8 000 000 gallons in 1956, and 19 665 000 gallons in 1957. During the first five months of 1958 12 376 000 gallons were produced.

The Minister said the figures indicate a steady increase which is expected to be maintained until the maximum annual production of 66 million gallons is reached. On the basis of 365 working days a year, SASOL is producing 90 300 gallons of petrol and fuel oil a day. The Union's present consumption (1957) is 426·5 million gallons yearly [*Afr. Econ. Newsletter* 26 July 1958].

SASOL should be in full production by 1960 when the rounding-off of the undertaking would be completed. There was also a gradual rise in the production of by-products which would eventually make SASOL the biggest chemical industry in the Southern Hemisphere.

The vast consolidation scheme costing about £4 million would be completed in two years. It would embody the erection of additional standby equipment of a major type, including boilers and synthesis reactors to enable the plant to function continuously.

The principle upon which this programme is based is that no further addition will be made to the capital structure of the Corporation, but that the

* For a description of this new establishment see W. REERINK and G. FEHLEMANN, 'Die neue Forschungsanstalt des Steinkohlenbergbaus'. *Glückauf* 94 (No. 39/40) (1958) 1430–35.

funds will be taken from the sale of SASOL products and, if necessary, from short-term loans.

Constant improvement had been achieved in SASOL's technical processes, so much so that people from Europe were coming to see how these processes work. South African scientists had to solve unique problems which no overseas experts could solve, Dr VAN RHIJN added. There was full confidence in the future of SASOL [State Information Service, Pretoria].

ISCOR expansion

The £3·5 million blast furnace at the Pretoria Works was blown in during July 1958. Production is rated at 10 000 short tons per week, compared with the combined weekly production of 12 500 short tons of the other three furnaces at Pretoria.

Other items already completed at the above works under the £56 million extensions programme include a coke oven battery (51 ovens) and a 65 to 70 ton electric arc furnace. Extensions and modernization of rolling mills, and erection of a new iron foundry are in hand.

At ISCOR Works, Vanderbijlpark, a third coke oven battery (51 ovens) and by-products plant, complete with coal handling facilities, is under construction. The installation of a 144 in. plate mill with finishing facilities has been commenced and in addition two Hoag rotor steel plants, one at each works, with a combined rated capacity of 600 000 ingot tons per annum are under construction.

Expansion at Thabazimbi iron ore mine includes an underground crushing plant. The gyratory crusher weighing 88 tons is rated to handle 8 000 tons of ore per day.

The current expansion programme is estimated to increase annual ingot production by 900 000 tons, and the rated capacity of the two works combined to 2 350 000 per annum [*Iscor News* March 1958].

THE NETHERLANDS

The gas industry in The Netherlands

It is expected that the collective Dutch gas undertakings, with the inclusion of the coking plants, will have delivered in 1958 about $1\,650 \times 10^6$ tetramecal*). This amount does not include direct deliveries from the oil companies to the industry in the form of propane and butane, and to domestic users in the form of butane in small steel bottles.

About 38 per cent of the above mentioned gas deliveries comes from the coking plants, 6 per cent being accounted for by mineral gas and 1 per cent by propane and butane. The other 55 per cent is produced by gas companies largely from solid starting products (about 1/10 of the output is made from gaseous and 1/20 from liquid materials).

There are indications, however, that in 1958 and 1959 the contribution of pure mineral gas to the supply will rise beyond the present 6 per cent level while, moreover, the gas companies will start using gaseous materials on a

* By tetramecal is understood an amount of gas which, upon combustion, yields 4 000 kcal, or 15 867 B.Th.U. (gross calorific value) and hence corresponds to approximately 1 m³ of town gas.

larger scale. A provisional calculation shows that in the future about 40 per cent of the national gas requirements will be covered from the latter source. Good distribution of the surpluses of gaseous energy in certain areas has been entrusted to the Nationale Gas Maatschappij which has just been established.

In 1958, as in other recent years, the Wobbe number has been adopted more and more as a quality indication of the gas instead of using the calorific value alone. In fact, the Wobbe number is now used so widely in The Netherlands that its standardization may soon be expected. The Committee 'Kwaliteitseisen voor Gas' has done much pioneering work in this field and intends to give an account of its activities at a special meeting.

The length of the Dutch transport grid for coke oven gas is over 800 km, that for mineral gas over 1 600 km. The main lines are for the greater part provided with cathodic protection, but the distribution lines in the various service areas are not.

It may be of interest to note that about 7 per cent of the new service lines in the various areas are of PVC.

First international congress for coal petrology

The First International Congress for Coal Petrology was held at Heerlen on 10 to 13 September 1958. There were 82 participants from 21 countries, among whom were several from the U.S.S.R. and other Eastern European countries. The 23 lectures covered three main subjects: (*1*) General coal petrography, (*2*) Applied coal petrography, and (*3*) Carboniferous sporology.

Drs YABLOKOV, VALTZ and GINSBURG (U.S.S.R.) reviewed the work done by Russian coal petrologists the results of which will be brought together in coal petrographical atlases for the separate coal basins. Some of these atlases were demonstrated at the Congress.

Successful attempts to prepare 1·3 micron thick polished sections of many coals were reported. Professor MACKOWSKY (Germany) gave an account of the activities of the international working group for coal petrographical analysis whose object it is to determine the relative value of various methods. Dr ALPERN (France) reported on the work done by the International Committee for the Nomenclature of Coal Petrology which has led to the compilation of a trilingual (French, German, English) glossary and to greater uniformity in nomenclature. Dr MURCHISON (Great Britain) confirmed the practical value of the Berek photometer by determining accurately the magnitude of the subjectivity factor of the measurements. Dr HACQUEBARD (Canada) demonstrated the value of a quantitative separation of vitrinite into telinite and collinite for the petrography of coking coals. This subject was also mentioned by Drs YABLOKOV and BOJOLINBOVA (U.S.S.R.) in their coal classification survey. Dr FEYS (France) discussed the occurrence of marine algae in coals. Drs TAYLOR and WARNE (Australia) gave an account of some coal petrological studies made in Australia.

The physical properties of a number of vitrains and durains were discussed by Dr VETTER, and an introduction to the development of applied coal petrology in the U.S.A. was given by Dr CADY.

Professor VAN KREVELEN (Neth.), speaking for his colleagues dealt with the pyrolytic properties of maceral concentrates from which the properties of the pure macerals can be derived. Dr JACOBS (D.D.R.) discussed the use of coal petrology as a means for improving the quality of coke from lignites. Dr KÖTTER (Germany) gave a survey of the methods and the quantitative microscopic analysis for improving briquetting processes.

The growing stratigraphic significance of carboniferous sporology was clearly demonstrated by seven authors.

Fourth international congress for carboniferous stratigraphy and geology

From 15 to 20 September 1958 the Fourth International Congress for Carboniferous Stratigraphy and Geology was held at Heerlen. The members, over 200, came from 20 countries. Compared with the previous Congress (1951) there appeared to be much greater interest from the U.S.S.R., Poland, Czechoslovakia and Yugoslavia.

The morning sessions during the Congress were devoted to: (*1*) paleontology; stratigraphy and orogenesis, (*2*) sedimentology, (*3*) applied geology, and (*4*) coal petrology, coal genesis and palynology.

Lectures were given by Prof. STOCKMANS (Belgium) on the paleobotanical work of the last seven years and its stratigraphical implications; by Prof. ELIAS (U.S.A.) on the marine fauna of North America and Europe; by Prof. RUTTEN on sedimentation and orogenic phases in the Carboniferous; by Dr POTTER (U.S.A.) on the origin of carboniferous sand-stones in Illinois; by Dr FISK (U.S.A.) on sedimentation in the Missisippi delta; by Dr JESSEN (Germany) on sedimentation in the Carboniferous with special emphasis on the paralic basins; by Prof. GORSKI (U.S.S.R.) on the organization, methods and results of geological investigations of the Carboniferous in the U.S.S.R.; by Ing. MONOMAKHOFF (France) on the effect of lateral tectonic movements on the calculation and exploitation of coal resources; by Prof. STACH (Germany) on the results of seven years of coal petrological investigations; by Dr M. TEICHMÜLLER (Germany) on the present knowledge of coal genesis; and by Dr ALPERN (France) on the palynological work of the International Congress for Coal Petrology (previous note).

In the afternoons 50 short papers were delivered.

Furthermore, there was a discussion of the answers received to a questionnaire by the late Prof. JONGMANS on the desirability and possibility of a correlation between regional and more general classifications of the Carboniferous.

A subcommittee for the Carboniferous was instituted under the auspices of the general Stratigraphical Committee of the International Geological Congress. Under the chairmanship of Dr VAN LECKWIJCK (Belgium) this subcommittee will study stratigraphical problems and make recommendations for the International Geological Congress.

The proceedings of the Congress will appear at the beginning of 1960. In addition to the lectures and discussions, the proceedings will also contain those papers which, owing to lack of time, could not be read at the Congress.

Letters to the Editor

Letters to the Editor on points of scientific interest related to fuel science are invited. The Editor does not hold himself responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Dehydrogenation of Coal and Tar Formation

RECENTLY the authors[1] have studied dehydrogenation of coal by sulphur and thereby have indicated the presence of significant amounts of alicyclic* carbon in coal. Alicyclicity (proportion of carbon in alicyclic form) has been found to decrease with increase in rank of coal. In the course of this work it was also observed that dehydrogenation of coal leads to almost complete inhibition of the formation of tar. This has been found to be true for all ranks of coal. This fact obviously raises the question as to the mechanism of formation of tar during pyrolysis of coal. It has been shown earlier that dehydrogenation can be carried out at 200° to 360°C, i.e. below the normal decomposition temperature of coal and that the only significant change which is brought about in the structure of coal is apparently the aromatization of the alicyclic part. It has also been established that during pyrolysis of the dehydrogenated material, an 'extra' amount of carbon (which almost corresponds to the alicyclic carbon) is found to be retained in the char over and above the usual amount found by Gray–King assay. The additional yield of char from dehydrogenated coal has been found to increase proportionately with the alicyclicity of coals. The yield of methane hydrocarbons for any coal, however, remains practically the same for the dehydrogenated coal compared to pyrolysis of the untreated coal. Evidently the carbon, which normally should have appeared in the form of tar, remains fixed in the char consequent on dehydrogenation.

The above findings lead to a direct relationship between the alicyclic part of coal structure and tar formation. The values of alicyclic carbon (*Table 1*) determined by dehydrogenation with sulphur (A. VESTERBERG'S method[2]) are found to be nearly equal as well as proportional (*Figure 1*) to the yields of tar. [The method of calculation of alicyclic hydrogen and hence of carbon from the amount of sulphuretted hydrogen formed due to dehydrogenation only has been shown[1] earlier, and the values thus obtained and presented here have also been found to be supported by a hydrogen balance of the original coal and its dehydrogenated product. Further, these values of alicyclic carbon have also been shown[1] almost to correspond to the 'extra' amount of carbon, referred to above, retained in the char at 600°C of dehydrogenated coal.]

The above relationship between yield of tar and alicyclic carbon of coal will appear significant as carbon in tar constitutes 90 per cent of its

* The terms 'hydroaromatic' and 'hydroaromaticity' used in an earlier paper[1] seem to be inappropriate as the nature of the reduced rings is not known at the moment and as such the authors replace these by the terms 'alicyclic' and 'alicyclicity' which are more general.

weight. It would appear, therefore, that the alicyclic part of coal is responsible for the formation of tar and dehydrogenation leads to inhibition of tar formation by modifying the structure. This view receives further support from the fact that anthracite, where no alicyclic carbon can be detected, does not yield any tar.

The above findings may also explain the carbonization behaviour of weathered or oxidized coals as well as halogenated coals. Such coals, as is known, yield little or no tar. Oxidation or weathering of coals has been found to lead to apparent destruction of the alicyclic structure as no dehydrogenation could be effected by reaction of sulphur with such coals. As to halogenated coals, it has also been shown[3] recently that a similar type of dehydrogenation and presumably aromatization of alicyclic carbon occurs through halogenation as in the sulphur reaction.

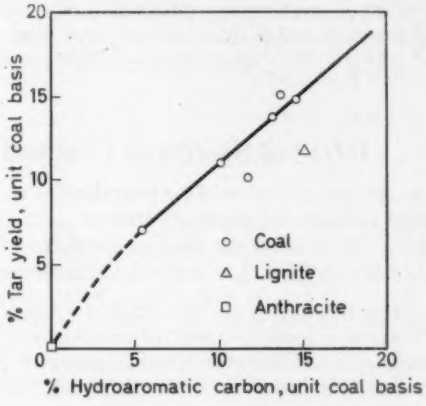

Figure 1. Relation between hydroaromatic carbon and tar yield

Table 1. Tar yield and hydroaromatic carbon in coal

Coal*	On unit coal, per cent			
	C	H	*Tar yield*	*Char*
1. *Lignite*	70·1	5·1	11·8	15·0
2. *Ranapariapur*†	81·1	5·5	14·8	14·6
3. *Samla*	82·2	5·4	13·8	13·2
4. *Dishergarh*	84·0	5·7	16·0	13·7
5. *Laikdih*†	87·3	5·3	11·0	10·1
6. *Jharia X*	90·1	5·0	10·1	11·7
7. *Madhuband IX*	90·3	4·63	7·0	5·5
8. *Anthracite (S. Wales)*	93·2	3·50	*Nil*	*Nil*

* The data for these coals have been presented earlier[1] except for Nos. 5 and 7.
† Vitrains.

Lastly, it is of interest to recall in this connection the findings of A. PICTET and L. RAMSEYER[4] on the nature of vacuum tar obtained from the Montrambert bituminous coal. The tar was found to be essentially alicyclic, and

no aromatic hydrocarbons or phenols were found. Observations of other authors[5] on vacuum distillation of coal are, however, somewhat different. In spite of these differences, oil and tar obtained under vacuum distillation have been found to be predominantly alicyclic.

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(*Received October 1958*)

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Infra-red Spectra of Coal and Some Coal Derivatives

A RECENT article[1] in *Fuel* contained a report on the i.r. spectra of various coal extracts. Of the many spectra given there, two are of particular interest here. These are of the benzene extracts of Coal No. 2, a sub-bituminous coal, and of Coal No. 3, a low-volatile bituminous coal.

The authors state that aromatic esters are responsible for most of the features in these two spectra and they imply that these extracts are therefore rich in 'adventitious or admixed components' of the coals, such as resins and waxes. Furthermore, they distinguish between selective and non-selective solvents largely by comparing the greater amount of structural detail in these two spectra with the more diffuse spectra obtained with other solvents. While I agree that the spectra indicate aromatic esters, I suggest that a large part of these extracts originated from a source other than the coal samples.

The i.r. spectrum of a benzene extract of 'Tygon' plastic tubing is reproduced in *Figure 1*. This spectrum matches perfectly with that of butyl

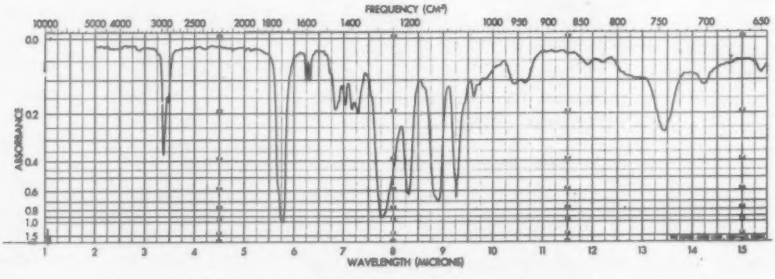

Figure 1. Infra-red spectrum of benzene extract of 'Tygon' plastic tubing

phthalyl butyl glycolate[2], which also seems to be identifiable by peaks at 5·78, 6·25, 6·32, 7·8, 8·9, 9·3, 9·6, 10·4, 10·6, 13·5 and 14·2 microns in the two coal extract spectra[3]. On several occasions we have obtained the same spectrum when examining benzene or carbon tetrachloride extracts which have come in contact even briefly with 'Tygon' tubing. The coal extract spectra show the presence of additional non-aromatic C—H bonds by increased absorption at 3·4, 6·85 and 7·25 microns. Wax is indicated in the spectrum of the Coal No. 2 benzene extract by weak absorption at about 13·7 and 13·9 microns. The presence of high molecular weight aromatics in the extract of Coal No. 3 is shown by increased absorption at 6·25 and 14·25 microns and by peaks at about 3·3, 6·65, 11·4, 12·3 and 13·4 microns.

The 'Tygon' tubing extract from which the above spectrum was obtained was prepared by swirling 2·1 g of tubing in a small beaker with 10 ml of reagent grade benzene for five minutes at room temperature. The tubing was then removed and the benzene was evaporated off by gently heating. The oily residue was pressed between two rock salt windows and the spectrum was scanned with a Perkin–Elmer Model 21 spectrophotometer.

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[2] See *NRC–NBS Infrared Compound Card No. 91* and *242* or *Sadtler Standard Spectrum No. 5285*

[3] The coal extracts may contain dibutyl phthalate, a widely used plasticizer, rather than butyl phthalyl butyl glycolate. Spectra of these esters are quite similar; see *Sadtler Standard Spectrum No. 1902*

Aromaticity of Coal—an Appraisal

IN the last few years it has been increasingly recognized that the basic structure of coal is essentially aromatic, and therefore attempts to determine the aromaticity of coal have been made from various approaches, such as X-ray[1], i.r.[2] and, in particular, D. W. VAN KREVELEN and H. A. G. CHERMIN's statistical structural analysis[3] and similar methods[4]. Recently the authors have looked at the problem from the chemical standpoint. Studies on oxidation of coal in air have led to the postulation of a mechanism[5] wherein the non-aromatic part of coal structure can be selectively oxidized under low temperature conditions (below 200°C), leaving the aromatic skeleton unaffected. As a result, determination[6] of aromatic carbon and, hence, of the 'aromaticity' is possible, and such values[6, 7] have been shown to be more or less consistent with those obtained from the statistical[3] and graphical densimetric[7] approaches. Further, the mechanism has led to successful determination of aromatic and non-aromatic hydrogen[9] in coal.

Since then, D. W. VAN KREVELEN *et al.*[10] have revised the earlier graphical densimetric method in the light of recent data[11] on pitch. This has enhanced the aromaticity values by about 10 per cent over the earlier ones. Consequently, the values obtained from the oxidation studies will now be found to be about 10 per cent too low. This obviously raises a question as to the validity of the mechanism of oxidation. The authors have, in the meantime, made further studies[7] on the mechanism, but have been unable to reconcile the discrepancy between the two sets of estimates.

A critical study of van Krevelen's recent work indicates that the revision of his earlier statistical relationship (between molar volume per carbon atom M_c/d, atomic H/C ratio and aromaticity) has been primarily based on the tacit assumption that pitch has 100 per cent aromaticity. In a preliminary study of the elementary composition of pitch this estimate for its aromaticity appeared to be too high. With 91·6 per cent carbon and 5·0 per cent hydrogen for a typical composition of a pitch fraction[10], no hypothetical model structure having 100 per cent aromaticity could be made which conforms at the same time to its elementary composition. This naturally suggests further work on the constitution of pitch.

Recent dehydrogenation studies[12] on coal made by the authors prompted them to examine pitch as well. A few samples of pitch having almost the same compositions as those of van Krevelen were treated for dehydrogenation by sulphur (Vesterberg's method), and it was found that pitch is as readily amenable to dehydrogenation as coal at 200° to 360°C. The reaction starts at 200°C and dehydrogenation appears to be complete after 2 to 3 h and at about 360°C. The sulphuretted hydrogen formed was trapped in ammoniacal cadmium chloride solution and estimated. Results of a typical dehydrogenation experiment with pitch are presented in *Tables 1* and *2* along with other relevant data.

*Table 1. Dehydrogenation of pitch (Gray–King assay apparatus)**

Amount, g		*Reaction temp. °C*	*Yield† of dehydrogenated pitch g*	*CdS (equivalent to H_2S) formed, g*	*Amount, g*			*Amount of carbon in pitch taken, g*	*Hydroaromaticity, C_{har}/C*
Pitch (d.a.f.)	S				H (*equivalent to H_2S*)	*Hydroaromatic*			
						H_{har}	C_{har}		
4·9	2·00	200° *to* 360°C	5·40	4·25	0·058	0·116 (0·058 × 2 = 0·116)	0·696 (0·116 × 6)	4·5	0·15

* No liquor was formed; gas, however, other than sulphuretted hydrogen was about 200 cm³ at n.t.p. (details to be published elsewhere).
† This includes free, imbibed and/or fixed sulphur; see *Table 2*.

Table 2. Constitution and properties of pitch and its dehydrogenated product

Sample	C %	H %	N %	S %	O% (*by diff.*)	d_4^{20}	(M_c/d_4^{20}) *corr.*	$\frac{H}{C}$
Pitch	92·04	4·88	1·20	0·58	1·30	1·241	10·35	0·636
Dehydrogenated pitch	80·56	2·47	1·10	14·61*	1·26	—	—	0·368

* See first footnote under *Table 1*.

It will be seen that pitch reacts with sulphur to a considerable extent and the ease with which it undergoes dehydrogenation at the lower temperatures indicates that it cannot be of 100 per cent aromatic character. It is well known that the aromatic hydrogen of a system is not removed under this condition. On the other hand, as has been shown earlier with coal[12], the amount of sulphuretted hydrogen formed may be taken as a measure of hydroaromatic hydrogen and hence hydroaromatic carbon (assuming, of course, the methylene groups to be largely unsubstituted). These values for hydroaromatic carbon and hydrogen (*Table 1*) also appear to be confirmed by an ultimate analysis balance of the original pitch and its dehydrogenated product. Thus, the hydroaromaticity (C_{har}/C) found for the particular sample was 0·15. Values for other samples range from 0·10 to 0·15. (A detailed study on the constitution of pitch will be published elsewhere.) Hence the aromaticity of pitch would be of the order of 85 to 90 per cent; at least it cannot be more than 90 per cent. On the other hand it may be even a little less than suggested, e.g. if aliphatic groups[13] are present.

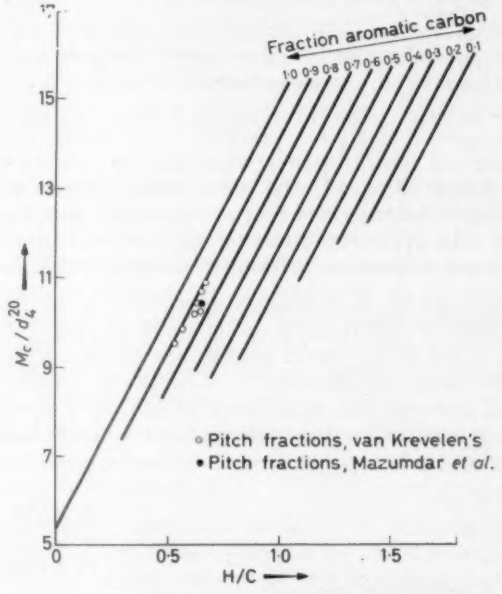

Figure 1. Determination of aromaticity (present authors' modification of figure due to D. W. VAN KREVELEN)

In view of the above findings, the revised M_c/d versus H/C graph of van Krevelen *et al.*[10] obviously needs further revision to obtain a better estimate for the aromaticity of coal. The authors have redrawn this relationship (*Figure 1*) in the light of their work on pitch referred to above. It will be seen that, except for revision of the pitch line, the other general principles adopted by van Krevelen were followed in constructing the diagram. In doing so,

it was found that extrapolation of 85 to 90 per cent aromaticity lines from the upper part of the curve (which represents well defined organic compounds) to the lower region clearly incorporates the data of pitch fraction given by van Krevelen[10], conforming at the same time to the experimental values for the aromaticity of pitch obtained by the dehydrogenation work. In contrast, it will be found that adoption of 100 per cent aromaticity for pitch necessitated

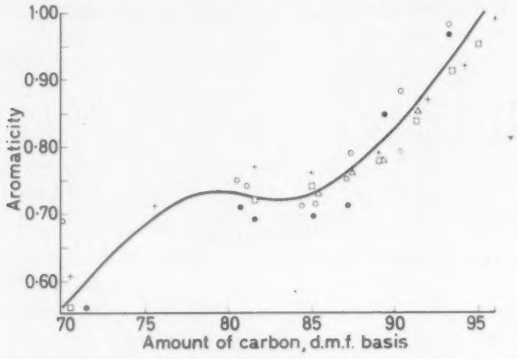

Figure 2. Comparison of aromaticity values by different methods

bending the aromaticity line in the lower regions for van Krevelen's latest work[10]. It is remarkable to find that the graphical densimetric method as revised by the authors practically restores van Krevelen's original graph[8] with which aromaticity data obtained from the oxidation method are consistent.

Thus, an appraisal of van Krevelen's recent work in the light of our study on pitch justifies the validity of his earlier approach (where the 100 per cent aromaticity line was drawn on the basis of benzene and graphite) and hence reconciles the apparent discrepancy between his recent estimates of aromaticity of coal and that determined by us from a chemical approach. These values of aromaticity from statistical and oxidation methods will also be found in general to be consistent with i.r. and other approaches[14] (*Figure 2*).

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Calculation of the Molecular Volumes of the Liquid Forms of Polycyclic Aromatic and Perhydroaromatic Hydrocarbons

RECENT attempts to estimate the fraction of aromatic carbon, f_a, in coals have been based on graphical representations of volume/composition relations. Calculation of f_a from these relations depends on the establishment of a line representing molecular volume per carbon atom, M_c/d, as a function of atomic hydrogen/carbon ratio, H/C, for the liquid forms of compounds containing 100 per cent aromatic carbon atoms. It was first assumed[1] that a straight line connecting the point for M_c/d for graphite with one for this quantity for benzene correctly represented 100 per cent aromaticity. In a later treatment[2] points for the liquid forms of benzene, naphthalene, anthracene and phenanthrene were located by extrapolating from the M_c/d values for the alkylated forms of these compounds, which are liquids, to the M_c/d corresponding to the value of H/C of the parent aromatic. In the most recent publications[3] other points on the 100 per cent aromatic carbon line have been established by assuming that the carbon in certain pitches and pitch fractions is entirely aromatic.

The purpose of the present communication is to describe a general method for calculating the molecular volumes of the liquid forms of aromatic and perhydroaromatic hydrocarbons.

The method depends upon two facts: (*1*) In aromatic hydroaromatic series of hydrocarbons the atomic volume of the added hydrogen is approximately constant, and (*2*) the volumes of ring increments in various liquid polycyclic perhydroaromatic compounds can be evaluated from available data.

The values of the atomic volume of hydrogen in the series: benzene–*cyclo*hexane, naphthalene–decalin, phenanthrene–perhydrophenanthrene, chrysene–perhydrochrysene, and diphenyl–di*cyclo*hexyl, have been calculated[4] and show a satisfactory degree of concordance. For these series it is, respectively: 3·35, 3·42, 3·50, 3·42 and 3·43 ml. Earlier workers[5] have recommended the value 3·4 ml, and in the calculations in this paper this value has been used.

The experimental values of molecular volumes on which our calculations of ring increments in liquid polycyclic perhydroaromatic compounds are based are shown in *Table 1.*

In condensed systems a new ring can be formed by adding 4, 3 or 2 carbon atoms. The molecular volume increment due to ring formation by a 4-carbon addition was calculated from a plot of molecular volume as a function of the

Table 1. Molecular volumes of perhydroaromatic compounds based on experimental densities

Compound	*Density**	*Mol. vol., ml*
cyclo*Hexane*[6]	0·7781	108·2
*Di*cyclo*hexyl*[7]	0·8846	188·0
Decalin		
cis[8]	0·895	
trans[9]	0·872	156·6†
Perhydrophenanthrene[10]	0·9423‡	204·0
Perhydropyrene[11]	0·9828	222·2
Perhydrochrysene[12]	0·9827	250·8
Perhydrotriphenylene[13]	0·9425	261·4

* All at 20°/4° except perhydropyrene, which is 25°/4°.
† Based on an average density of 0·883.
‡ Average of 3 values.

number of rings for the compounds *cyclo*hexane, decalin, perhydrophenanthrene and perhydrochrysene. The equation of this line was found to be $M_v = 61{\cdot}1 + 47{\cdot}5N$, where M_v is molecular volume, N is the number of rings, and 47·5 ml is the increase in volume for a 4-carbon increment in this series.

The molecular volume increment due to ring formation by the addition of 3 carbon atoms was obtained by taking half the difference between the molecular volumes of perhydropyrene and the average value for decalin; this is 32·8 ml. Similarly, a molecular increment due to 2-carbon atom addition, 18·2 ml, is obtained from the difference in molecular volumes of perhydropyrene and perhydrophenanthrene.

An idea of the internal consistency of the data can be obtained by comparing calculated and experimental values for the compounds listed in *Table 1.* The calculated value for decalin based on the experimental value for *cyclo*hexane plus the 4-carbon increment is 155·7; those for perhydrophenanthrene based on *cyclo*hexane, decalin and di*cyclo*hexyl, 203·2, 204·1 and 206·2; those for perhydropyrene, based on *cyclo*hexane, decalin, di*cyclo*hexyl and perhydrophenanthrene, are 221·3, 222·2, 224·4 and 222·2 and for perhydrochrysene based on *cyclo*hexane, decalin, perhydrophenanthrene, and di*cyclo*hexyl 250·7, 251·6, 251·5 and 253·6. In general, the agreement between calculated and experimental values for these compounds is within 1 per cent. However, for perhydrotriphenylene, the discrepancy is greater. Calculations for this compound, based on the experimental values for *cyclo*hexane, decalin, di*cyclo*hexyl and perhydrophenanthrene, lead to values of 250·7, 251·6, 253·7 and 251·5, respectively, compared with the experimental value of 261·4—a difference of about 3 per cent.

To calculate the molecular volume of the liquid form of a compound such as perhydrocoronene one can start with the experimental values for any of the compounds of *Table 1* except perhydrochrysene. The average value obtained by this procedure is 306·3. By a similar procedure and using 306 for the molecular volume of perhydrocoronene, the molecular volume of perhydroovalene is found to be 390.

To obtain the values for the liquid forms of the parent aromatics it is necessary to subtract from the molecular volume of the perhydro compound the atomic volumes of the hydrogen atoms added to the aromatic in forming the perhydro compounds. Following this procedure and using 3·4 ml for the atomic volume of hydrogen, the molecular volumes for the liquid forms of coronene and ovalene are found to be 224 and 281, respectively.

Other methods[14] of estimating molecular volumes of the liquid forms of normally solid aromatic hydrocarbons, such as extrapolation of the values of density from above the melting point or determination of partial molal volume from solutions, are available but also subject to uncertainty. However, comparisons with such values are of interest and are shown in *Table 2*. The present method of calculation leads to values that are consistently some 2 per cent lower.

Table 2. Comparison of molecular volumes of aromatic compounds by several methods[14]

Compound	*Solution**	*Extrapolation*†	*Calculation*‡
Naphthalene	125·0	124·9	122·6
Biphenyl	—	149·2	147·2
Phenanthrene	159·0	159·8	156·4
Pyrene	172·0	—	168·0

* In a eutectic of α- and β-naphthalene.
† From the *d* at about the melting point.
‡ Based on the experimental values of the perhydro compounds and atomic volume of hydrogen of 3·4 ml.

It is evident that this method can be applied generally to cyclic compounds; but, as in all such methods, the farther the extrapolation from experimental data, the less confidence can be placed in the results.

Application of the data obtained by this procedure to the study of coal structure has already been discussed briefly[4] and will be treated at greater length in a later communication.

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(*Received October 1958*)

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A Note on Constant Volume Coal Sampling

CONSIDER a population of coal particles classifiable into k classes and define for $i = 1 - k$,

N_i = proportion by number of particles,
V_i = proportion by volume,
W_i = proportion by weight,
v = small volume,
w = small weight,
v_i = integer, such that $(v_i v)$ is particle volume,
w_i = integer, such that $(w_i w)$ is particle weight,
d_i = density,
a_i = ash proportion,

so that,

A = (ash proportion in population) $= \Sigma(N_i w_i a_i)/\Sigma(N_i w_i)$
$V_i = (N_i v_i)/\Sigma(N_i v_i)$
$W_i = (N_i w_i)/\Sigma(N_i w_i)$.

If, now, a sample of coal particles is taken from this population, A is estimated by $\hat{A}$ where $\hat{A} = x/y$, x being the weight of ash and y the total weight of the sample. The problem then is to determine the variance of $\hat{A}$, given the relevant population data, and R. C. TOMLINSON [*Fuel, Lond.* 36 (1957) 442] has recently discussed one situation in which, if n_i be the number of particles of the ith class occurring in the sample, it is assumed that the n_i are independent and such that $E(n_i) = KN_i$, where K is a constant. It is then shown that $V(\hat{A}) = \Sigma W_i(w_i w)(a_i - A)^2/M$, where M is the expected sample weight, and this formula is the well known one due to Kassel and Guy. As Tomlinson suggests, the assumptions are most likely to obtain when the sample is scraped off, in a standardized manner, from a conveyor belt moving at a constant speed and such that neither volume nor weight of the sample will remain constant.

CONSTANT VOLUME SAMPLE

However, an even more usual procedure approximates to the taking of constant volume samples, this volume generally being substantially larger

than that of the largest particle volume, and it is of interest, therefore, to consider the variance of $\hat{A}$ which would result from this procedure.

Consider, then, a sampling process in which a volume (Vv), considered in imagination as comprising V ordered cells each of volume v, is located at random in the population volume of coal, and that volume (Vv) is extracted as the sample. Assume for the moment that (Vv) is so large relative to the largest ($v_i v$) that the error here due to the necessary inclusion of whole particles is negligible. The estimate of A is $\hat{A} = x/y$ where $x = \Sigma x_j$ and $y = \Sigma y_j$, x_j being the ash content and y_j the total weight of the jth cell of the sample volume.

Now, assuming that the population of particles is well mixed ('randomized') one has, considering the jth cell,

$$\begin{aligned}
E(x_j) &= \Sigma V_i(vd_i a_i) = \bar{M}A \\
E(y_j) &= \Sigma V_i(vd_i) = \bar{M} \\
V(x_j) &= \Sigma V_i(vd_i a_i - \bar{M}A)^2 \\
V(y_j) &= \Sigma V_i(vd_i - \bar{M})^2 \\
W(x_j y_j) &= \Sigma V_i(vd_i a_i - \bar{M}A)(vd_i - \bar{M})
\end{aligned}$$

for all $j = 1 - V$. These random variables x_j (and y_j) are not, however, independent. Considering two subscripts m, n selected at random from $1 - V$, the probability of m referring to a volume of a particle of the ith class is V_i and the probability of n referring to a volume of the same particle $(v_i - 1)/(V - 1)$, so that the total probability of m and n referring to volumes of the same particle is $p_V = \Sigma V_i(v_i - 1)/(V - 1)$.

Then, it is readily seen that

$$V(x) = V[1 + (V - 1)p_V]\Sigma V_i(vd_i a_i - \bar{M}A)^2$$

and since the factor $[1 + (V - 1)p_V]$ can be reduced to $\Sigma(V_i v_i) = \bar{v}$ one has

$$V(x) = V\bar{v}\Sigma V_i(vd_i a_i - \bar{M}A)^2$$

and, similarly,

$$\begin{aligned}
V(y) &= V\bar{v}\Sigma V_i(vd_i - \bar{M})^2 \\
W(xy) &= V\bar{v}\Sigma V_i(vd_i a_i - \bar{M}A)(vd_i - \bar{M})
\end{aligned}$$

Since now

$$\begin{aligned}
E(x) &= V\bar{M}A = MA \\
E(y) &= V\bar{M} = M
\end{aligned}$$

the use of the usual formula for the variance of a ratio gives

$$\begin{aligned}
V(\hat{A}) &= V\bar{v}\Sigma V_i(vd_i)^2(a_i - A)^2/M^2 \\
&= \Sigma W_i(\bar{v}vd_i)(a_i - A)^2/M \\
&= \Sigma W_i(\bar{v}/v_i)(w_i w)(a_i - A)^2/M
\end{aligned}$$

DISCUSSION

The formula given above differs in general from that of Kassel and Guy, but will be the same in the special case when the particles are all of equal volume. Evidently, this variance will be greater or less than that under the conditions

proposed by Tomlinson depending upon how ash and density vary in relation to particle size.

Furthermore, it may be noted that the formula will be exact if, apart from the population being well mixed and there being no air spaces,

(*a*) the volume of the sample is exact cutting across particles where they intersect the sample boundaries,

(*b*) the value of p_V refers to the population of particles generated by the extraction of an infinite number of samples, as in (*a*) above, from the population.

These conditions will not be realizable in practice, but the formula should be the best available for what purports to be a constant volume sample, just as Kassel and Guy's formula is probably best under the conditions Tomlinson proposes.

However, it is agreed with Tomlinson that these formulae are more of theoretical interest than of practical use, and that only direct sampling investigations can produce convincing evidence as to variances.

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(*Received November 1958*)

PAPERS ACCEPTED FOR FUTURE PUBLICATION

The following papers have been accepted for publication in future issues of FUEL

THE DEPENDENCE OF THE ELASTIC BEHAVIOUR OF COAL ON THE MICROCRACK STRUCTURE. *N. B. Terry*

THE CHLORINATION OF LOW RANK COALS WITH (*a*) SULPHURYL CHLORIDE, AND (*b*) HYDROGEN PEROXIDE–HYDROCHLORIC ACID. *F. J. Pinchin*

THE DETERMINATION OF PHOSPHORUS IN COAL ASH. *R. J. Cosstick and H. N. S. Schafer*

THE VARIABILITY OF VITRINITES IN BRITISH COAL SEAMS. *L. H. Leighton*

CHEMICAL STRUCTURE AND PROPERTIES OF COAL XXII—BEHAVIOUR OF INDIVIDUAL MACERALS AND BLENDS IN THE AUDIBERT–ARNU DILATOMETER. *D. W. van Krevelen, H. N. M. Dormans and F. J. Huntjens*

CHARACTERIZATION OF PITCHES FOR CARBON ANODES. *M. B. Dell*

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